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CATIONIC NITRILE DERIVATIVES OF MANGANESE CARBONYL

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled

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ABSTRACT

The nitrosonium ion, NO^+, has been used as an oxidizing agent in the synthesis of cationic manganese carbonyl nitriles. The metal-metal bond in $Mn_2(CO)_{10}$ has been oxidized by nitrosonium hexafluorophosphate in nitrile solution, and solvent coordination employed to prepare a series of nitrile containing cations of the form $[RCNMn(CO)_5]^+[PF_6]^-$ (R = Me, n-Pr, t-Bu, Ph). A similar reaction with trans-$Mn_2(CO)_8(PR_3)_2$ (PR_3 = PPh_3, $P(OPh)_3$, $PMePh_2$) produced only the cis-$[RCNMn(CO)_4PR_3]^+[PF_6]^-$. A mechanism for this reaction has been proposed. The infrared and Raman spectra of these cations have been studied.

The hexacarbonyl cations, $[M(CO)_6]^+[PF_6]^-$, have been prepared by the oxidation of $M_2(CO)_{10}$ (M = Mn, Re) in nitromethane solution; solvent coordination cannot occur in this case. This reaction is consistent with the proposed mechanism.

The reactions of these cationic nitriles have been studied; the CO and RCN groups appear to be inert with respect to substitution reactions. However, the salt $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$ has been prepared. Only one MeCN group in this salt is labile in substitution reactions, and can be replaced by various ligands to form cations of the form cis-$[(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$. The stereochemistry of this reaction has been studied.

ACKNOWLEDGEMENTS

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SYNTHESIS OF SOME CATIONIC NITRILE DERIVATIVES OF MANGANESE

CARBONYL

Introduction

The rapid development of synthetic organometallic chemistry has been largely directed towards the preparation of neutral and anionic complexes. Cationic metal carbonyl complexes are relatively few in number. One reason for this lies in the inherent ionic nature of such complexes, making their separation and characterization somewhat more difficult than neutral complexes. The techniques of sublimation, mass spectroscopy and chromatography cannot be readily employed, and the polar solvents required for infrared work makes characterization more difficult.

The first metal carbonyl cation to be reported was $[Co(CO)_3(PPh_3)_2]^+[Co(CO)_4]^-$, as recently as 1958[1]. Various methods have been employed to synthesise cationic metal carbonyl derivatives[2]. A brief outline of these methods is presented with particular reference to Mn and Re.

The parent metal carbonyl cations, $[M(CO)_6]^+$, have been prepared by halide displacement from $M(CO)_5X$ at high temperatures and pressures in the presence of a Lewis acid to promote halide abstraction.

$$M(CO)_5X + AlCl_3 + CO \longrightarrow [M(CO)_6]^+[AlCl_3X]^-$$
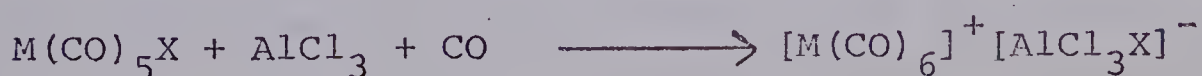
M=Mn, 90°C, 300 atm, 20 hours[3,4,5,6].

M=Re, 90°C, 320 atm, 20 hours[5,6,7,8].

The hexacarbonyl cations have also been prepared by acid-
ification of the alkoxyl derivative.

$$M(CO)_5COOEt \xrightarrow{\text{dry HCl}} [M(CO)_6]^+ [HCl_2]^- + EtOH \quad (9,10)$$
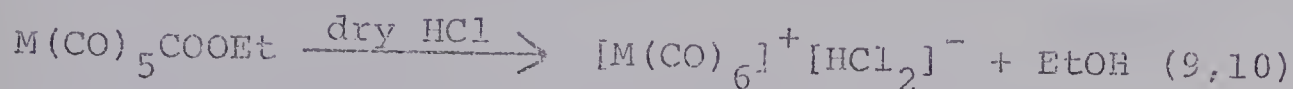
Substituted hexacarbonyl cations have been pre-
pared from the corresponding pentacarbonyl halide by carb-
onylation[3,4,5,6].

$$Mn(CO)_4(PPh_3)Cl \xrightarrow{AlCl_3/CO} [Mn(CO)_5(PPh_3)]^+ [AlCl_4]^- \quad (4,5)$$

$$Mn(CO)_3(PPh_3)_2Cl \xrightarrow{AlCl_3/CO} [Mn(CO)_4(PPh_3)_2]^+ [AlCl_4]^- \quad (5,6)$$
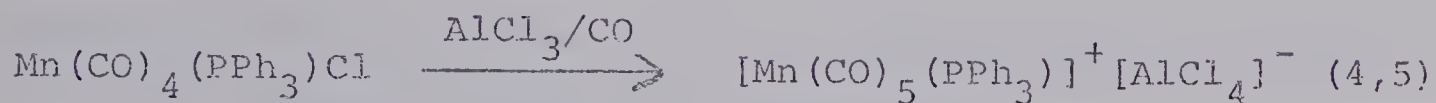
A pressureless synthesis for this disubstituted salt is
also available.

$$Mn(CO)_3(PPh_3)_2Cl \xrightarrow[CO]{AlCl_3/C_6H_6} [Mn(CO)_4(PPh_3)_2]^+ [AlCl_4]^- \quad (5)$$
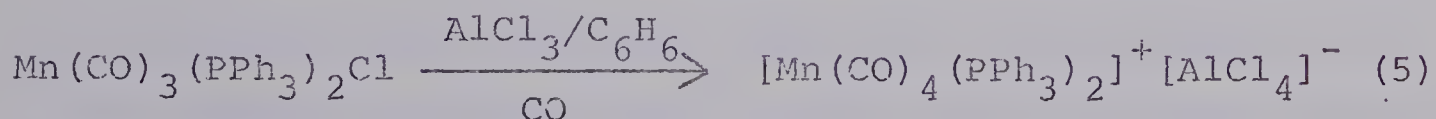
The ease of halide displacement in these reactions is facil-
itated by the use of polar solvents, and by decreasing
carbonyl substitution; the following order is observed,
Cl>Br>I; Mn>Re.

The direct replacement of halide has been employed
in a few cases, or displacement of CO from other cations.

$$Mn(CO)_5Cl + NH_3 \longrightarrow [Mn(CO)_{6-n}(NH_3)_n]^+ Cl^-$$
$$n=2^{11}, 3^{12}.$$

$$[Mn(CO)_5(C_2H_4)]^+ + PPh_3 \longrightarrow [Mn(CO)_4(PPh_3)_2]^+ \qquad (13)$$

$$[Re(CO)_6]^+[ClO_4]^- + v\text{-triars} \longrightarrow [(v\text{-triars})Re(CO)_3]^+$$
$$[ClO_4]^- \qquad (14)$$
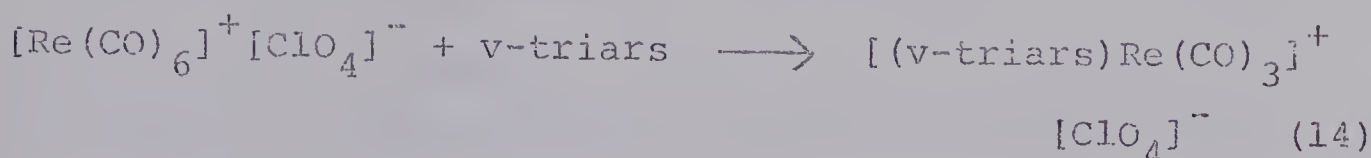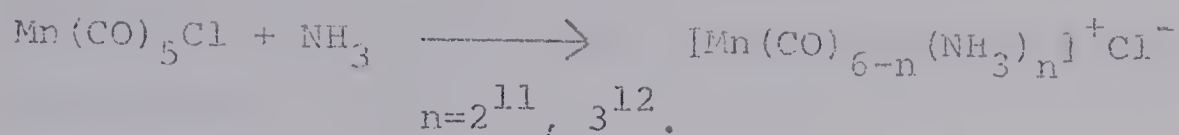
v-triars = tris-1,1,1-(dimethylarsinomethylethane).

Arene derivatives can be prepared from $Mn(CO)_5X$ by using arene instead of CO.

$$Mn(CO)_5X + AlCl_3 + arene \longrightarrow [(arene)Mn(CO)_3]^+[AlCl_4]^-$$
$$arene = C_6H_6 \ (16), \ C_4Me_4S \ (17).$$
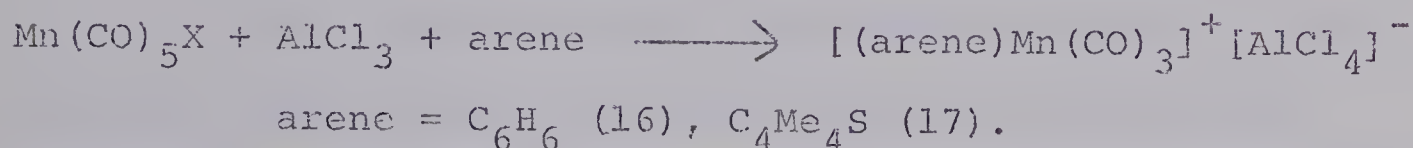
Such arene groups are readily replaced by other ligands[18]. The synthesis of other cations of this type is reported by Abel and Tyfield[2].

Recently, a method of preparation of metal carbonyl cations has been developed using the nitrosonium ion as a one electron oxidizing agent. Since the nitrosonium ion was used in this work to prepare cations, a brief discussion of its reactions is presented.

The use of the nitrosonium ion, NO^+, as a reagent in transition metal chemistry has been largely confined to the preparation of nitrosyl derivatives. Relatively few workers have employed the nitrosonium ion as an oxidizing agent.

The nitrosonium ion is isoelectronic with carbon

monoxide and has been used to form transition metal nitrosyl derivatives in the following ways.

$$Ir(CO)(PPh_3)_2Cl \xrightarrow[C_6H_6,MeOH]{NOBF_4} [Ir(CO)(PPh_3)_2(NO)Cl]^+[BF_4]^- \quad (19)$$

$$h^5-C_5H_5Re(CO)_3 \xrightarrow[hot\ CH_2Cl_2]{NOHSO_4} [h^5-C_5H_5Re(CO)_2(NO)]^+[HSO_4]^- \quad (20)$$

$$M(CO)_6\ (M=Cr,Mo,W) \xrightarrow[MeCN]{NOPF_6} [M(MeCN)_4(NO)_2]^{2+}[PF_6]^- \quad (21)$$

$$Fe(CO)_3(PPh_3)_2 \xrightarrow{NOPF_6} [Fe(CO)_2(PPh_3)_2(NO)]^+[PF_6]^- \quad (22,23)$$
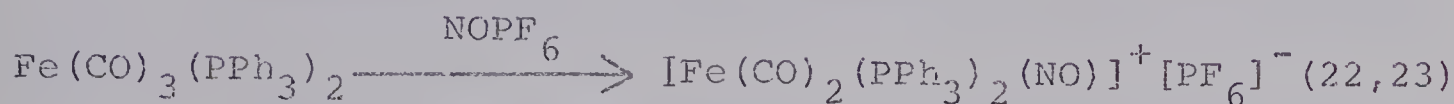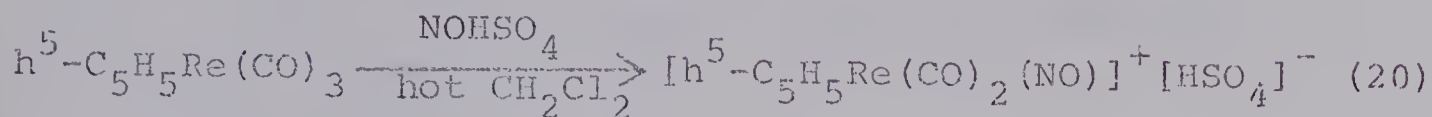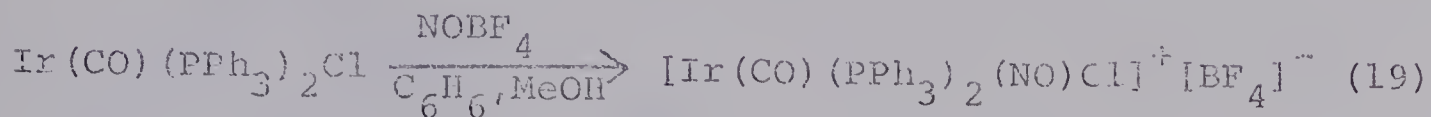
The reactions of NO^+ with metal carbonyls, particularly those of group VIB, and with the various metal carbonyl anions, have been extensively studied by Okamoto[21]. That work was essentially directed towards obtaining nitrosyl derivatives and was not intended as a study of the oxidizing nature of the NO^+ ion.

The highest occupied molecular orbital in nitric oxide, NO, is antibonding in character, and contains a single electron. This electron can be removed to form the nitrosonium ion, NO^+; the ionization potential is 9.5eV. The nitrosonium ion can therefore act as a powerful oxidizing agent. The ion was first used as an oxidizing agent in transition metal chemistry by Hathaway and Underhill[24,25]. They oxidized pure metals in acetonitrile solution to form M^{II}-acetonitrile complexes, where M = Fe,Co,Cu and Ni.

The nitrosonium ion has been used to advantage for

the oxidation of nickel salts containing complex ligands.
High yields are reported[26].
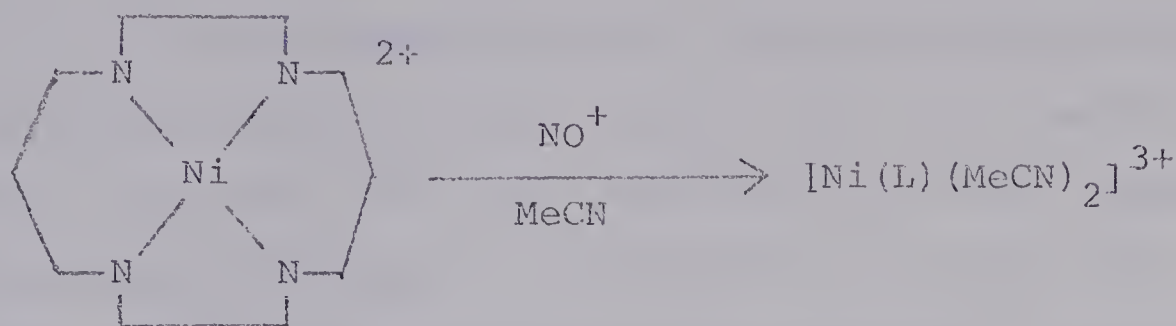
L = 1,4,8,11-tetraazacyclotetradecane (cyclam).

Ferrocene can also be oxidized to the ferricinium ion[27].

The NO^+ ion has recently been employed as a one electron oxidant in metal carbonyl chemistry. The nature of the ligands present in the carbonyl derivatives and the solvent system appear to be critical in these reactions. If solvents of low coordinating ability are used, such as methylene chloride or benzene, solvent coordination can be avoided[28].

$$\underline{cis}\text{-Mo(CO)}_2\text{(DPE)}_2 \xrightarrow[CH_2Cl_2]{NOPF_6} trans\text{-[Mo(CO)}_2\text{(DPE)}_2]^+ [PF_6]^-$$

$$\underline{trans}\text{-Mn(CO)}_3\text{(DPE)Br} \xrightarrow{NOPF_6} cis\text{-[Mn(CO)}_3\text{(DPE)Br]}^+ [PF_6]^-$$

$$(DPE = Ph_2PCH_2CH_2PPh_2)$$
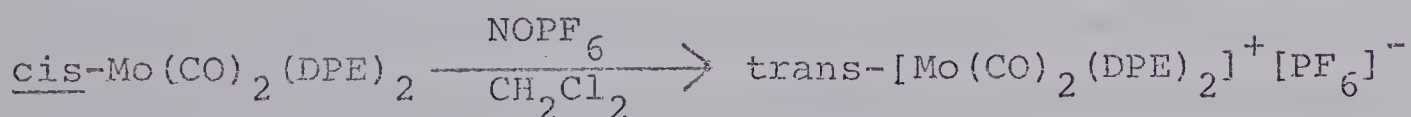
However, the use of MeOH/toluene as a solvent system for $NOPF_6$ can result in hydride formation[27], possibly due to formation of HPF_6 by reaction with MeOH.

$h^5-C_5H_5Ir(CO)PPh_3 \xrightarrow{\hspace{3cm}} [h^5-C_5H_5Ir(CO)PPh_3(H)]^+[PF_6]^-$
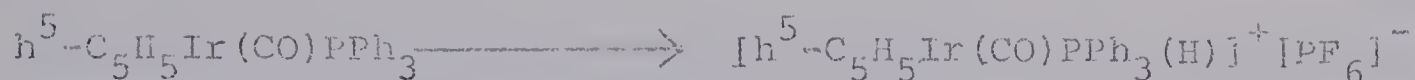
The nitrosonium ion has not been used extensively in binuclear metal carbonyl systems where metal-metal bond fission can occur, with the evolution of NO gas. Okamoto[21], and subsequently Connelly and Dahl[29], have found that $M_2(CO)_{10}$ (M = Mn,Re) could be oxidized by NO^+ in acetonitrile solution to give complexes of the type $[MeCNM(CO)_5]^+[PF_6]^-$. Cations can only be obtained directly from $M_2(CO)_{10}$ in a few cases.

$$M_2(CO)_{10} + DPE \xrightarrow[\text{Dioxane}]{100°C} [Mn(CO)_2(DPE)_2]^+[Mn(CO)_5]^- \quad (30)$$

$$M_2(CO)_{10} + BuNH_2 \xrightarrow{\hspace{3cm}} [Mn(CO)_5(BuNH_2)]^+[Mn(CO)_5]^- \quad (15)$$
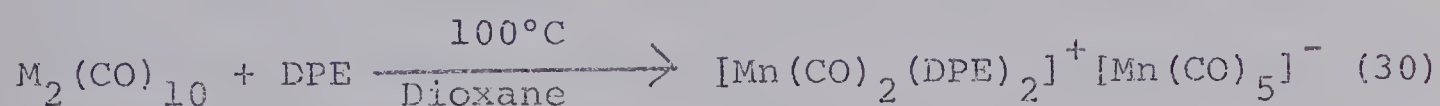
The basis of this work was to employ NO^+ as an oxidant of the metal-metal bond in $M_2(CO)_{10}$. By using a series of nitrile solutions of NO^+, solvent coordination can be used to prepare a series of cationic nitrile derivatives of the form $[RCNMn(CO)_5]^+[PF_6]^-$. The reaction has been extended to include derivatives of the type $[RCNMn(CO)_4PR_3]^+$ $[PF_6]^-$, obtained from the starting material trans-$Mn_2(CO)_8$ $(PR_3)_2$. Cationic nitrile derivatives of manganese are unavailable by other methods, as are disubstituted cations in which the substituents are different.

The phosphine substituted nitrile derivative is of a cis configuration, and this allows a mechanism for the

oxidation to be proposed. The mechanism can be further eluc-
idated using nitromethane as a solvent, since no solvent
coordination can then occur. The product of the reaction is
then $[M(CO)_6]^+[PF_6]^-$.

Results and Discussion

The reaction of nitrosonium hexafluorophosphate
with $Mn_2(CO)_{10}$ in RCN solvent (R = Me, n-Pr, t-Bu, Ph) gives
products of stoichiometry $[RCNMn(CO)_5]^+[PF_6]^-$. These com-
pounds are air-stable crystalline solids, soluble in meth-
ylene chloride, acetone, nitromethane and nitriles. The
solutions are stable with respect to air oxidation over sev-
eral days. Conductivity measurements in nitromethane give
molar conductivities of the order of 85 mhos cm^2 $mole^{-1}$.
This is close to the average value of 83 mhos cm^2 $mole^{-1}$ for
a 1:1 electrolyte in nitromethane[31]. Analysis confirms the
formulation.

A similar reaction in nitromethane provides the
known cation $[Mn(CO)_6]^+[PF_6]^-$. Presumably nitromethane can-
not form a stable complex in the same fashion as the nitrile
solvents, and carbon monoxide stabilizes the intermediate.
The CO is probably a product of decomposition.

The compound trans-$Mn_2(CO)_8(PR_3)_2$ (PR_3 = PPh_3,
$P(OPh)_3$, $PMePh_2$) reacts with $NOPF_6$ in nitrile solution to
produce yellow crystalline derivatives, stable in air and in
solution, of stoichiometry $[RCNMn(CO)_4PR_3]^+[PF_6]^-$. Conduct-
ivity measurements in nitromethane indicate a 1:1 electrolyte,

the formulation being confirmed by analysis.

In general, the salts are prepared by the addition of $NOPF_6$ in RCN in a dropwise fashion to a suspension of $Mn_2(CO)_{10}$ or trans-$Mn_2(CO)_8(PR_3)_2$ in the same solvent. A slow addition is necessary to prevent any substantial formation of $[Mn(CO)_6]^+[PF_6]^-$. After the nitrile solvent is removed under reduced pressure, the product can be extracted from excess $NOPF_6$ with methylene chloride, with the exception of $[MeCNMn(CO)_5]^+[PF_6]^-$. The limited solubility of this compound in methylene chloride necessitates the use of an exact 2:1 molar ratio of $NOPF_6$ to $Mn_2(CO)_{10}$. Generally the $NOPF_6$ is added over several hours, the solution changing colour from yellow to light green, due to the presence of excess $NOPF_6$. During the course of the addition, NO is evolved. The pure salts are obtained by crystallization from acetone/diethyl ether. The $P(OPh)_3$ and $PMePh_2$ derivatives could not be obtained in crystalline form. Attempted crystallization from methylene chloride/n-hexane, methylene chloride/diethyl ether, acetone/diethyl ether and nitromethane/diethyl ether provided oils. The $[MeCNMn(CO)_4PMePh_2]^+$ $[PF_6]^-$ derivative can be analysed as an oil, but the corresponding phosphite salt gives unsatisfactory analytical results. Infrared data for representative samples are recorded in Table III. The cationic manganese carbonyl nitriles are diamagnetic and conform to the 'rare gas formalism' of metal carbonyls[32,33].

If the nitrile R group is considered a point lig-

and and only the CO frequencies considered, the cis product has C_s symmetry and group theory predicts four infrared active CO vibrations (3A'+A"). The trans derivative would possess C_{4v} symmetry and exhibit two infrared active bands (A_1+E). The infrared spectrum shows that the reaction is entirely stereospecific producing only the cis product. If the trans product is formed, then its rate of conversion to the cis compound must be faster than its rate of formation.

Mechanism

The reaction of $NOPF_6$ with trans-$Mn_2(CO)_8(PR_3)_2$ to produce only the cis product allows a reaction mechanism to be postulated.

During the course of the reaction, no nitrosyl stretching modes are observed in the infrared, indicating that no substantial formation of a nitrosyl complex is occurring unless its rate of reaction is much greater than its rate of formation.

A possible mechanism involves the oxidative cleavage of the metal-metal bond to produce a five coordinate cation and a five coordinate radical (Fig. 1). The other product of the reaction is NO which escapes from the system as gas. The radical can dimerize to reform the starting material or be oxidized further by NO^+ to form the cation. This cation is necessarily square-pyramidal at first, a geometry imposed by the structure of the dimer. Immediate reaction with the solvent would produce trans-$[RCNMn(CO)_4PR_3]^+[PF_6]^-$.
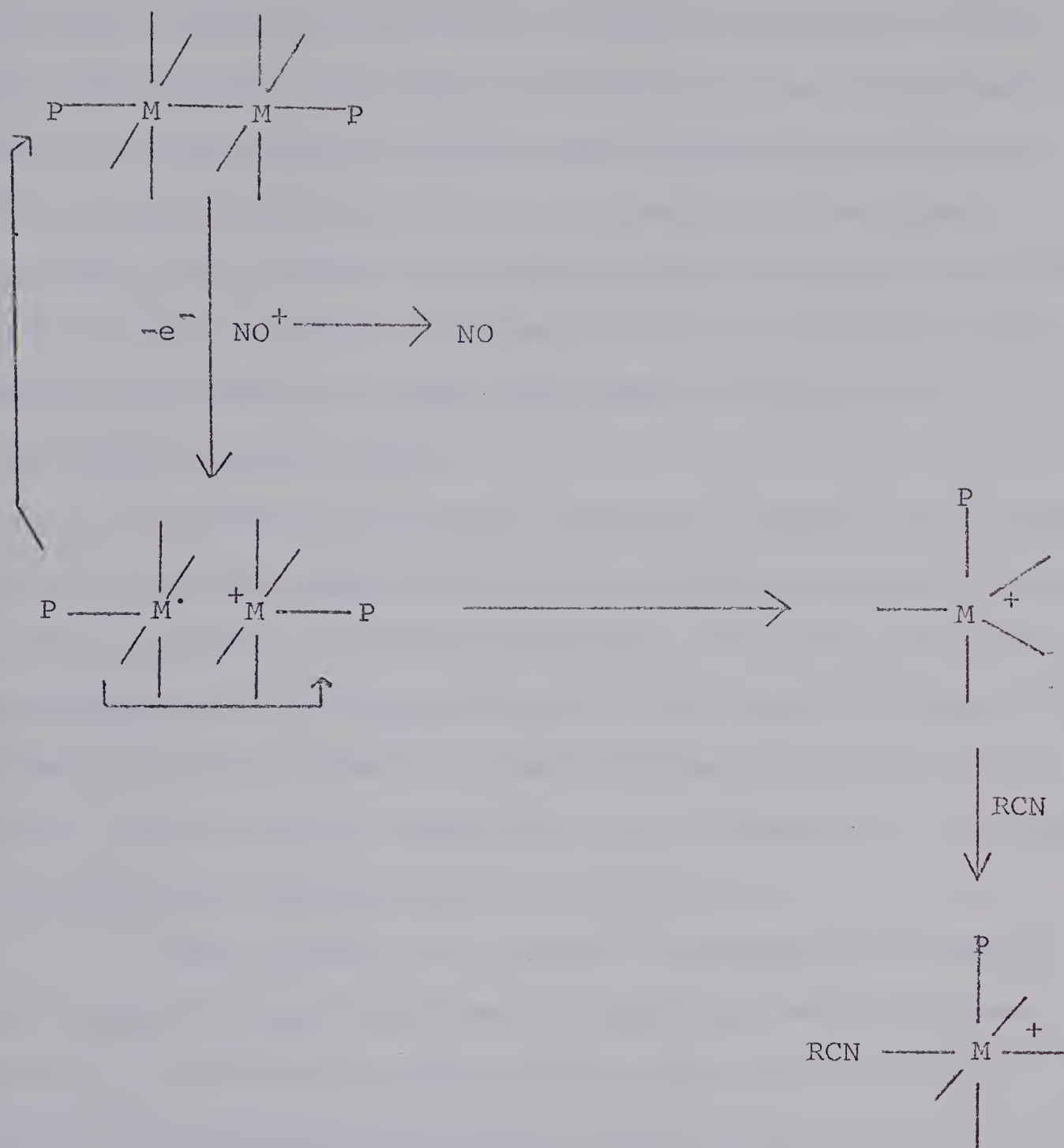
FIGURE I

Mechanism of the oxidation of $M_2(CO)_{10}$ and trans-$Mn_2(CO)_8$ -

$(PR_3)_2$. The CO groups are omitted for clarity; P = PR_3.

However, if the cationic intermediate has a reasonably long lifetime, transformation into a trigonal-bipyramidal structure could occur since this is unlikely to be a high energy process. The phosphine ligand would probably be axial in this trigonal-bipyramid since it is axial in the square-pyramidal form. Attack by nitrile on this trigonal-bipyramidal structure is likely to occur at the least hindered site, namely the equatorial plane. This would then produce cis-$[RCNMn(CO)_4PR_3]^+[PF_6]^-$.

A second alternative mechanism involves the initial formation of the trans derivative by immediate attack on the square-pyramidal cationic intermediate, followed by a rapid rearrangement to the cis product on the basis of thermo-dynamic stability. Such a transformation would have to be rapid, since no extra bands that may correspond to the trans derivative are observed in the infrared.

When $M_2(CO)_{10}$ (M = Mn,Re) is treated with NOPF$_6$ in a solvent of poor coordinating ability, such as nitro-methane, the initial product of the oxidation, $[M(CO)_5]^+$, cannot be stabilized by solvent coordination. Decomposition of this intermediate would then take place. This would prov-ide a source of CO, and this could stabilize the intermed-iate to form $[M(CO)_6]^+[PF_6]^-$. This product is in fact isola-ted from the reaction in reasonable yield and is consistent with the proposed mechanism. In the case of $[Mn(CO)_6]^+PF_6]^-$, nitromethane is present in the solvation sphere and cannot be removed by drying under high vacuum for 2 days. This

reaction provides a more convenient method of preparation of the $[M(CO)_6]^+[PF_6]^-$ derivatives than the high temperature, high pressure synthesis from $M(CO)_5X$ and AlX_3 (X = halogen)[5]. A small increase in yield of the $[M(CO)_6]^+[PF_6]^-$ salts can be obtained by bubbling CO through the reaction mixture as the $NOPF_6$ is added (Mn = 45%; Re = 40%).

The reaction of $[h^5-C_5H_5Fe(CO)_2]_2$ and $[h^5-C_5H_5Mo-(CO)_3]_2$ with $NOPF_6$ in acetonitrile gives similar products to the reaction of the manganese system, namely $[h^5-C_5H_5Fe(CO)_2-(MeCN)]^+[PF_6]^-$ and $[h^5-C_5H_5Mo(CO)_2(MeCN)_2]^+[PF_6]^-$. Reaction of "iron dimer" in a poorly coordinating solvent such as methylene chloride produces $[h^5-C_5H_5Fe(CO)_3]^+[PF_6]^-$. This is similar to the reaction of $M_2(CO)_{10}$ in nitromethane, and is consistent with the proposed mechanism.

Infrared and Raman Spectra

The compounds $[n-PrCNMn(CO)_5]^+[PF_6]^-$ and $[n-PrCN-Mn(CO)_4PPh_3]^+[PF_6]^-$ were chosen for a more detailed spectroscopic study. These compounds are readily soluble in methylene chloride, and the solutions are more stable to air oxidation than the corresponding MeCN analogues. However, the general principles obtained from the n-PrCN derivatives can be readily applied to the other members of the series.

If $[n-PrCNMn(CO)_5]^+[PF_6]^-$ is considered to be of octahedral geometry and consequently of C_{4v} symmetry, group theory predicts four infrared active stretching modes $(3A_1+E)$ and five Raman active modes $(3A_1+B_1+E)$. The ν_{CN}

stretching mode in the free nitrile is of the order 2250 cm^{-1}. The ν_{CN} is therefore expected to be of comparable energy to ν_{CO} and is included in the above stretching modes. Since the CN group lies on all the symmetry elements of the point group, the ν_{CN} will be of A_1 symmetry. It has been assumed that the nitrile group coordinates in an end-on rather than side-on fashion to the transition metal, in analogy to CO, CN$^-$, and RNC (R = alkyl or aryl) with which it is isoelectronic.

The infrared spectrum of $[n\text{-}PrCNMn(CO)_5]^+[PF_6]^-$ in methylene chloride indicates 4 ν_{CO} bands as expected of modified C_{4v} symmetry. The assumption that the Pr group be a point ligand is not strictly true for the purposes of determining band number by group theory. The asymmetry of the nitrile ligand tends to reduce the point group to C_1, allowing the formally inactive B_1 mode to become weakly active in the infrared.

When the infrared spectrum is recorded in a Nujol mull, the band at 2079 cm^{-1} in solution splits into 2 bands at 2086 and 2075 cm^{-1}. As the symmetry is reduced from C_{4v}, partial lifting of the degeneracy of the E mode would be expected so that this band can be considered to be the CO E mode. This band is very strong in the infrared and very weak in the Raman as expected.

In the Raman spectrum in methylene chloride solution, a very strong band is observed at 2115 cm^{-1}. This band can be assigned as the B_1 mode since it is very weak in

the infrared as expected of modified C_{4v} symmetry. What is more, this band is not polarized in the solution Raman, indicating that it is not of A_1 symmetry. The band at 2165 cm^{-1} is polarized indicating A_1 symmetry. The quality of the remainder of the spectrum is poor and further assignment is not possible. Nevertheless, if the E and B_1 modes are assigned then all the ν_{CO} are assigned, as shown in table I.

The location of the ν_{CN} stretch was not determined by Connelly and Dahl[29] nor by Okamoto[21] for the compound $[MeCNMn(CO)_5]^+[PF_6]^-$. The ν_{CN} stretch in the compound $MeCNM(CO)_5$ could not be located by Sheline for M = Mo,W[34]. However, if the infrared spectrum of a concentrated solution of $[n-PrCNMn(CO)_5]^+[PF_6]^-$ is measured in methylene chloride, two weak bands can be observed around 2300 cm^{-1}, one of which may correspond to the nitrile stretching mode. (The ν_{CN} in free n-PrCN is 2253 cm^{-1}.) This is inferred from work by Dunn and Edwards[35], who prepared complexes of the type $Mn_2(CO)_6X_2(MeCN)_2$, containing axial nitrile groups and halogen bridges. They observed two bands at 2320 and 2300 cm^{-1}, in addition to many ν_{CO} modes below 2100 cm^{-1}. The higher of these bands was assigned to ν_{CN} and the lower to a $\delta_{sym}(CH_3)$ + $\nu_{sym}(C-C)$ combination band. It therefore seems reasonable to extrapolate their results to this work, since the metal-nitrile system is so similar. No attempt is made to assign the ν_{CN} to one of these bands specifically. Recently, the ν_{CN} stretches in $[Cr(MeCN)_4(NO)_2]^{2+}[PF_6]^-_2$ have been assign-

ed at 2328 and 2300 cm^{-1}, and in $[(h^5-C_5H_5)_2V(MeCN)_2]^+[PF_6]^-$ at 2325 and 2350 cm^{-1} [27]. The nitrile stretch in the compound MeCNCr(CO)$_5$ has been assigned at 2291 cm^{-1} [36].

An explanation is now required for the increase in ν_{CN} upon coordination with the metal. Such an increase is apparently characteristic of nitriles bonded through the nitrogen lone pair of electrons [37]. Two factors should be included in the explanation.

As the nitrile bonds to the metal, the electronegativity of the nitrogen is increased. This slight change in the ionic character of the C-N bond would be expected to increase the C-N force constant. Similar arguments have been applied to the C-H bond [38]. There is also some evidence for an increase in the C-N force constant in the complexes BX$_3$.RCN (X = halogen) [39]. This argument cannot be extended indefinitely, since the bonding would then become electrostatic, and the force constant would be inversely proportional to the square of the distance between the atoms.

A second factor to consider is kinematic coupling of the C-N and M-N stretching modes, although the force constant may be unchanged from that of the free ligand. Some valence field calculations have been done on the RCNM system [40].

Back donation from the metal into π-orbitals of the the CN group cannot be used to explain the increase in ν_{CO} since only π^* orbitals are unfilled in RCN.

The assignment of element-nitrile nitrogen stretches has met with some controversy in the past, mainly because

TABLE I

Infrared and Raman Data

Compound		ν_{CN} $+(\delta_{symR}$ $+ \nu_{symC-C})$		ν_{CO} cm^{-1}			
$[(n\text{-PrCN})Mn(CO)_5]^+ [PF_6]^-$	a	2306(vw)	2293(vw)	2162(w)A_1 2117(w)B_1	2079(vs)E	2042(m)A_1	
	b	2306(vw)	2293(vw)	2162(w)	(2086,2075)(vs)	2046(m)	
	c	2308(m)	2318(w)	2165(m)	2080(vw)	2046(m)	
$[(n\text{-PrCN})Mn(CO)_4PPh_3]^+$ $[PF_6]^-$	a		2290(w)	2111(s)	2044(s)	2030(s)	1998(s)
	b		2300(w)	2114(s)	2047(s)	2035(s)	1995(s)
	c	2312(m)	2308(sh)	2116(s)	2053(s)	2036(m) 2031(sh)	1968 (m)
	d			562(s) 551(m) 523(s) 516(s) 505(m)	473(m)	431(m)	

^{a}Infrared in methylene chloride. ^{b}Infrared of Nujol mull.

^{c}Raman of solid. ^{d}Far infrared Nujol in polyethylene.

of the few recorded values of such vibrations. Dunn and

Edwards[35] assigned the Mn-N stretch in $Mn_2(CO)_6X_2(MeCN)_2$ at

230 cm^{-1}. Other values which have been recorded include:

174 cm^{-1}	for $ZnCl_2(MeCN)_2$	(41)
222 and 207 cm^{-1}	for $SnCl_4(MeCN)_2$	(42)
550-480 cm^{-1}	for $M(CO)_3(MeCN)_3$	(43)

Far infrared spectra of compounds of the type

$[RCNMn(CO)_5]^+[PF_6]^-$ would be expected to be similar to those

obtained by Dunn and Edwards since the systems are so similar.

However, no band is observed around 230 cm^{-1}, although many

bands are seen in the ν_{M-C}, δ_{MCO}, δ_{NCC} region. The positive

charge on the metal would be expected to raise the Mn-N

stretching frequency and appears to do so into a region

where assignment becomes difficult.

Assignment of the bands in the infrared and Raman

spectra of $[n-PrCNMn(CO)_4PPh_3]^+[PF_6]^-$ proves more difficult.

If the ligands are taken as point groups, the symmetry can

be estimated as C_s for the *cis* derivative and C_{4v} for the

trans compound. Group theory predicts the following for the

ν_{CO} stretching modes:

C_s 3A'+A"   all infrared active

C_{4v} A$_1$+B$_1$+E   the B$_1$ mode is Raman active only.

The band number corresponds to the *cis* isomer only. Even

when t-BuCN is chosen as solvent in an attempt to form the trans derivative, the cis isomer is formed, despite steric crowding. Attempts to identify the A" mode of the n-PrCN derivative by solution Raman work failed because the compound exhibits fluorescence in both methylene chloride and nitromethane.

It is interesting to note the ν_{CO} in (MeCN)Cr(CO)$_5$, the compound isoelectronic with [MeCNMn(CO)$_5$]$^+$[PF$_6$]$^-$. The infrared active bands are 2080(w), 1954(s) and 1930(m) cm^{-1} in n-hexane[44]. The bands of the cation, recorded in methylene chloride, are of the order of 100 cm^{-1} higher in frequency. This is a result of less M-COπ* bonding, imposed by the positive charge on the metal. This has the effect of strengthening the C-O bond and increasing the ν_{CO}.

The positions of the bands in [RCNMn(CO)$_5$]$^+$[PF$_6$]$^-$ appear to be independent of the nature of R. In the series [MeCNMn(CO)$_4$PR$_3$]$^+$[PF$_6$]$^-$, where PR$_3$ = PMePh$_2$, PPh$_3$ and P(OPh)$_3$, the band positions reflect the nature of the phosphine to a small extent. The best π-acceptor is the P(OPh)$_3$ ligand, decreasing the charge on the metal and the amount of M-COπ* bonding. The ν_{CO} are therefore highest in this compound. The worst π-acceptor of the three is PMePh$_2$, and consequently the ν_{CO} are lowest in this compound. The positions of the bands in which RCN varies with constant PR$_3$ again appear to be independent of the nature of the nitrile R group.

Conductivities

The molar conductivities of the products of the reaction of $NOPF_6$ with $Mn_2(CO)_{10}$ or trans-$Mn_2(CO)_8(PR_3)_2$ are of the order expected of 1:1 salts[31]. The salts are readily soluble in nitromethane without decomposition, and this provides a good solvent for measuring conductivities (table V).

NMR Spectra

Assignment of the bands in the ^{1}H NMR spectra of these compounds is routine. Chemical shifts are recorded in table IV. It is of interest to note the doublet observed for the Me group in the compound cis-$[MeCNMn(CO)_4PPh_3]^+[PF_6]^-$, produced by coupling with the phosphorus. The coupling, is, however, very weak (J_{P-H} = 3 c.p.s.).

EXPERIMENTAL

All reactions were carried out in a nitrogen atm-
osphere. Methylene chloride was dried over anhydrous magnes-
ium sulphate, n-hexane over sodium and acetonitrile distilled
from calcium hydride. Diethyl ether, acetone and nitromethane
were used as obtained from commercial sources.

Nitrosonium hexafluorophosphate was used as obtain-
ed from Ozark-Mahoning Chemicals. Manganese and Rhenium
carbonyls were obtained from commercial sources and used
without further purification.

Infrared spectra were measured using a Perkin-
Elmer 337 grating spectrometer and recorded in expanded form
on a Hewlett-Packard 7127A recorder. All spectra were re-
corded using 0.5 mm KBr or NaCl cells, and calibrated with
a carbon monoxide or polystyrene reference. Raman spectra
were recorded using a Carsons Laboratories model 10SP Ar^+/
Kr^+ laser, a Spex model 1401 monochromator, a cooled FW130
photomultiplier and photon counting electronics. The Kr^+
17,600 cm^{-1} line was used, and the spectra calibrated with a
CCl_4 reference. Far infrared work was undertaken on a Beck-
man IR-11 spectrometer. The Nuclear Magnetic Resonance
spectra were measured on a Varian A56/60 spectrometer, using
tetramethylsilane as an internal reference. All compounds
gave sharp NMR signals except were noted, and are thus pre-
sumed to be diamagnetic. Mass spectra were measured using

Associated Electrical Industries MS-9 and MS-12 instruments, using direct introduction of solid sample and source temperatures of about 100°C.

Melting points were recorded on a Kofler hot stage. Microanalyses were performed by the microanalytical laboratory of this department.

Molar conductivities were measured with a Philips PR9500 bridge, using nitromethane as solvent. A cell with stainless steel electrodes and cell constant of 1.4 (at 25°C) was employed. A constant temperature bath was maintained at 25°C and each conductivity determined twice.

Preparation of trans-$Mn_2(CO)_8(PR_3)_2$; $PR_3 = PPh_3$, $P(OPh)_3$, $PMePh_2$.

Typically, $Mn_2(CO)_{10}$ (3.9g., 10 mmoles) and the phosphine or phosphite (25 mmoles) were dissolved in benzene (200ml) and irradiated for several hours using a 450 watt UV lamp. The reaction was carried out in a nitrogen atmosphere. When the solution no longer exhibited the infrared bands due to $Mn_2(CO)_{10}$, the solution was reduced to small bulk on a rotary evaporator and n-hexane added (100ml). Cooling to -20°c affords yellow crystals of $Mn_2(CO)_8(PR_3)_2$. The product was filtered off and washed with n-hexane (2 x 30ml). Recrystallization from benzene/n-hexane provides the product which was used without further purification.

Yields : PPh_3 74%, $P(OPh)_3$ 47%, $PMePh_2$ 55%.

IR data : PPh$_3$ 1980(sh), 1956(vs) in CH$_2$Cl$_2$[69].

P(OPh)$_3$ 2001(sh), 1983(vs) in CH$_2$Cl$_2$[69].

PMePh$_2$ 1978(sh), 1951(vs) in benzene.

Preparation of [MeCNMn(CO)$_5$]$^+$[PF$_6$]$^-$.

To a suspension of Mn$_2$(CO)$_{10}$ (3.9g.; 10 mmoles) in acetonitrile (50ml), nitrosonium hexafluorophosphate (3.5g., 20 mmoles) in the same solvent (30ml) was added through a dropping funnel over the course of two hours, during which time NO was evolved. The addition must be slow to avoid the formation of [Mn(CO)$_6$]$^+$[PF$_6$]$^-$. Excess NOPF$_6$ should not be used since separation problems are then encountered. During the course of the addition the solution changes colour from yellow to light green. The solvent was then removed under reduced pressure, leaving a cream-coloured powder. This mat-erial was then crystallized from acetone/diethyl ether, affording [MeCNMn(CO)$_5$]$^+$[PF$_6$]$^-$ in 90% yield.

Any increase in the concentration of Mn$_2$(CO)$_{10}$ or rate of NOPF$_6$ addition tends to increase the amount of [Mn(CO)$_6$]$^+$[PF$_6$]$^-$ formed. For example, 30 mmoles of Mn$_2$(CO)$_{10}$ in 100ml of solvent and an addition time of one hour pro-duces [Mn(CO)$_6$]$^+$[PF$_6$]$^-$ in 24% yield based on Mn$_2$(CO)$_{10}$.

Preparation of [RCNMn(CO)$_5$]$^+$[PF$_6$]$^-$; R = n-Pr, t-Bu, Ph.

To a suspension of Mn$_2$(CO)$_{10}$ (3.9g., 10 mmoles) in the nitrile solvent (50ml), nitrosonium hexafluorophosphate in the same solvent (50ml) was added through a dropping

funnel until gas evolution ceased (3 hours). During the
course of the addition at room temperature, the solution
changed colour from yellow to light green due to the pres-
ence of excess $NOPF_6$. Magnetic stirring was continued for
two hours. The solvent was removed under reduced pressure
leaving a yellow, oily solid. This solid was then extracted
with methylene chloride (50ml) and the remaining $NOPF_6$
removed by filtration. The methylene chloride was removed
using a rotary evaporator and the solid crystallised from
acetone/diethyl ether at -20°C after 24 hours. The mother
liquor was decanted and the yellow or cream crystals washed
with diethyl ether (2 x 15ml) and dried under vacuum. The
salts are air stable and decompose only slowly in solution
over a period of days. Analytical, spectroscopic and conduct-
ivity data are shown in tables II-V.

Preparation of $[RCNMn(CO)_4PR_3]^+[PF_6]^-$; R = Me, n-Pr, t-Bu, Ph;

$PR = PPh_3$, $P(OPh)_3$, $PMePh_2$.

Typically, excess $NOPF_6$ in the nitrile solvent
(50ml) was added in a dropwise manner to a suspension of
trans-$Mn_2(CO)_8(PR_3)_2$ (0.2g., 0.34 mmoles) in the same nitrile
(50ml) until gas evolution ceased. The reaction was followed
by infrared spectroscopy until the band due to $Mn_2(CO)_8(PR_3)_2$
disappeared. The solution was allowed to stir for two hours,
and the solvent removed from the light green solution under
reduced pressure. The excess $NOPF_6$ was removed by extracting
the product with methylene chloride (50ml) and filtering

through a medium-pore sinter. The methylene chloride was removed on a rotary evaporator, and the product obtained by crystallization from acetone/diethyl ether at -20°C after 24 hours. The liquid was decanted and the crystals washed with diethyl ether (2 x 20ml) and dried under high vacuum for 48 hours.

This method of isolation proved satisfactory for the triphenylphosphine derivatives, however, with triphenyl-phosphite and methyldiphenylphosphine as ligand, only oils could be obtained. Recrystallization from solvent systems such as methylene chloride/diethyl ether, methylene chloride /n-hexane and acetone/diethyl ether was also unsuccessful. Purification by chromatography could not be carried out, since the salts tended to be absorbed by the column material (florisil and silica gel). The compound $[MeCNMn(CO)_4PMePh_2]^+$ $[PF_6]^-$ was analysed as an oil after solvent had been removed under high vacuum for 7 days. Analysis of the oily $P(OPh)_3$ product proved unsatisfactory. These products, however, ex-hibited very similar infrared spectra to the fully character-ized PPh_3 derivative. Physical data are shown in tables II-V.

Preparation of $[M(CO)_6]^+[PF_6]^-$; M = Mn,Re.

To a solution of nitromethane (35ml) containing $M_2(CO)_{10}$ (1.0g), $NOPF_6$ in the same solvent (30ml) was added in a dropwise manner until gas evolution ceased. In the case of manganese, the yellow solution turned light green, and

with rhenium the solution turned dark red. Magnetic stirring
was continued for 60 minutes and then the solution reduced
to small bulk and poured into methylene chloride (100ml).
The white precipitate of $NOPF_6$ was removed by filtration
through a medium-pore sinter and the solution again reduced
to small bulk. Addition of diethyl ether (100ml) immediately
produced a precipitate of $[M(CO)_6]^+[PF_6]^-$. The liquid was
decanted and the solid washed with diethyl ether (2 x 20ml)
and dried under vacuum. Analytical data and physical prop-
erties are shown in tables II-V. In the case of the white
manganese derivative one mole of nitromethane remains in the
solvation sphere even after drying under vacuum (0.1 mm
Hg) for 48 hours.

TABLE II

Analytical Data and Physical Properties

Compound	Calculated %			Found %			% Yield[a]	Colour	M.P. °C
	C	H	N	C	H	N			
[MeCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	22.07	0.79	3.58	22.25	0.80	3.67	90	White	Dec 145
[n-PrCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	26.43	1.72	3.42	26.62	1.94	3.37	71	Yellow	Dec 145
[t-BuCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	28.39	2.14	3.31	28.43	2.44	3.69	20	Cream	Dec 117
[PhCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	32.53	1.14	3.16	32.38	1.21	3.30	60	White	Dec 120
[MeCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	46.84	2.94	2.27	46.84	3.24	2.43	55	Yellow	Dec 140
[n-PrCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	48.54	3.44	2.17	49.50	3.24	2.30	40	Cream	Dec 137
[t-BuCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	49.33	3.68	2.13	49.39	4.22	2.19	67	Cream	Dec 135
[PhCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	51.42	2.97	2.07	51.47	3.52	1.83	41	Cream	Dec 125
[MeCNMn(CO)$_4$PPh$_2$Me]$^+$[PF$_6$]$^{-b}$	41.25	2.92	2.53	40.93	3.85	2.53	..	Yellow	...
[Mn(CO)$_6$]$^+$[PF$_6$]$^-$·CH$_3$NO$_2$	19.60	0.71	3.27	19.43	0.78	2.81	40	White	...
[Re(CO)$_6$]$^+$[PF$_6$]$^-$	14.43	–	–	14.46	–	–	34	Cream	...

[a]Yield based on Mn$_2$(CO)$_{10}$ and trans-Mn$_2$(CO)$_8$(PR$_3$)$_2$.   [b]Analysed as an oil.

TABLE III

Infrared Data[a]

Compound	ν_{CN}'	$\nu_{C-C}+\delta_R$	ν_{CO} cm^{-1}			
[MeCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	2303(vw)	2287(vw)	2163(w)	2116(w)	2080(vs)	2043(m)
[n-PrCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	2306(vw)	2293(vw)	2162(w)	2117(w)	2079(vs)	2042(m)
[t-BuCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	2306(w,sh)	2293(w)	2162(w)	2117(w)	2079(vs)	2042(m)
[PhCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	2301(m)	2275(w)	2163(w)	2119(w)	2077(vs)	2045(m)
[MeCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	2325(w)	2292(w)	2112(s)	2044(s)	2030(s)	1995(s)
[n-PrCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	2290(w)		2111(s)	2040(s)	2030(s)	1998(s)
[t-BuCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	2290(vw)	2272(vw)	2111(s)	2043(s)	2027(s)	2003(s)
[PhCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	2269(w)	2258(w,sh)	2110(s)	2041(s)	2028(s)	2000(s)
[MeCNMn(CO)$_4$PPh$_2$Me]$^+$[PF$_6$]$^-$	...	...	2111(s)	2040(s)	2028(s)	1993(s)
[n-PrCNMn(CO)$_4$PPh$_2$Me]$^+$[PF$_6$]$^-$	...	...	2111(s)	2039(s)	2028(s)	1997(s)
[MeCNMn(CO)$_4$P(OPh)$_3$]$^+$[PF$_6$]$^-$	...	...	2125(m)	2062(s)	2042(s)	2012(s)
[Mn(CO)$_6$]$^+$[PF$_6$]$^-$·CH$_3$NO$_2$	...	...	2095(s)	in nitromethane		
[Re(CO)$_6$]$^+$[PF$_6$]$^-$	...	...	2086(s)	in nitromethane		

[a]Taken in methylene chloride, unless otherwise noted.

TABLE IV

^{1}H NMR Spectral Data[a]

Compound	τ[b]
[MeCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	7.70 singlet (Me)
[n-PrCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	8.95 triplet (Me), 8.20 complex (CH$_2$), 7.22 triplet (CH$_2$CN)
[t-BuCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	8.53 singlet (Me)
[PhCNMn(CO)$_5$]$^+$[PF$_6$]$^-$[c]	2.16 complex (Ph)
[MeCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	7.98 doublet (Me), 2.37 complex (Ph)
[n-PrCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	9.20 triplet (Me), 8.60 complex (CH$_2$), 7.62 triplet (CH$_2$CN)
[t-BuCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$[c]	8.73 singlet (Me), 2.32 complex (Ph), 2.42 complex (Ph)
[PhCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$[c]	2.35 complex (Ph)

[a]Recorded in CD$_2$Cl$_2$ unless otherwise noted.

[b]Refers to peak centres.

[c]Recorded in CD$_3$COCD$_3$.

TABLE V

Conductivity Data[a]

Compound	Solution conc. (mM)	Conductivity (mhos cm^{2}mole^{-1})	Temperature (°C)
[MeCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	0.91	75.1	25.2
[n-PrCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	1.13	95.7	25.0
[t-BuCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	0.97	84.9	25.2
[PhCNMn(CO)$_5$]$^+$[PF$_6$]$^-$	1.05	82.1	25.0
[MeCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	1.17	85.5	24.8
[n-PrCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	0.93	91.6	24.8
[t-BuCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	1.10	80.0	25.2
[PhCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$	0.95	77.6	24.8

[a]Measured in nitromethane.
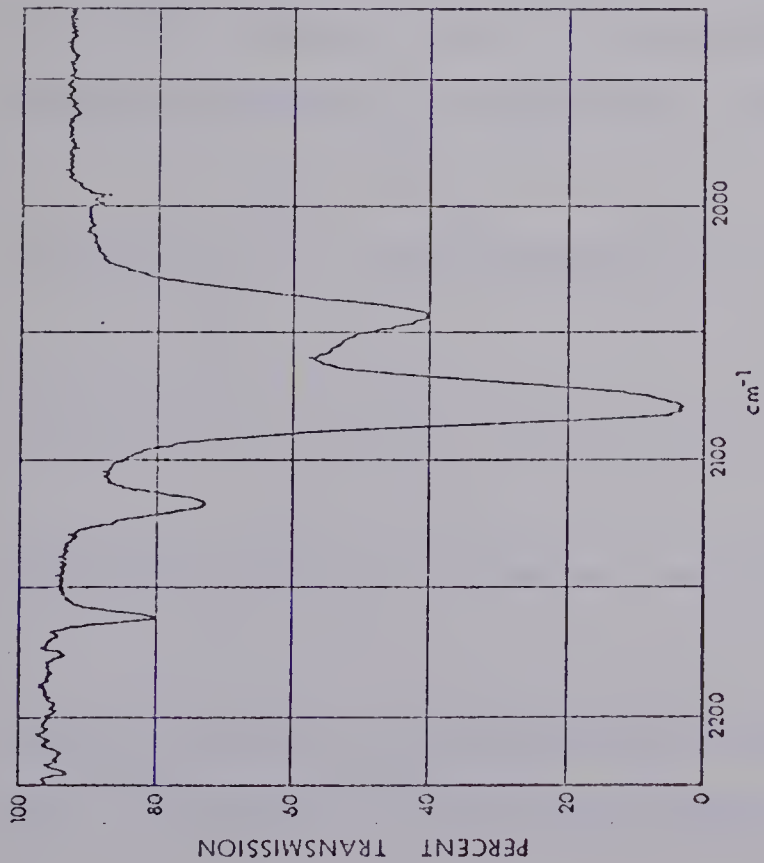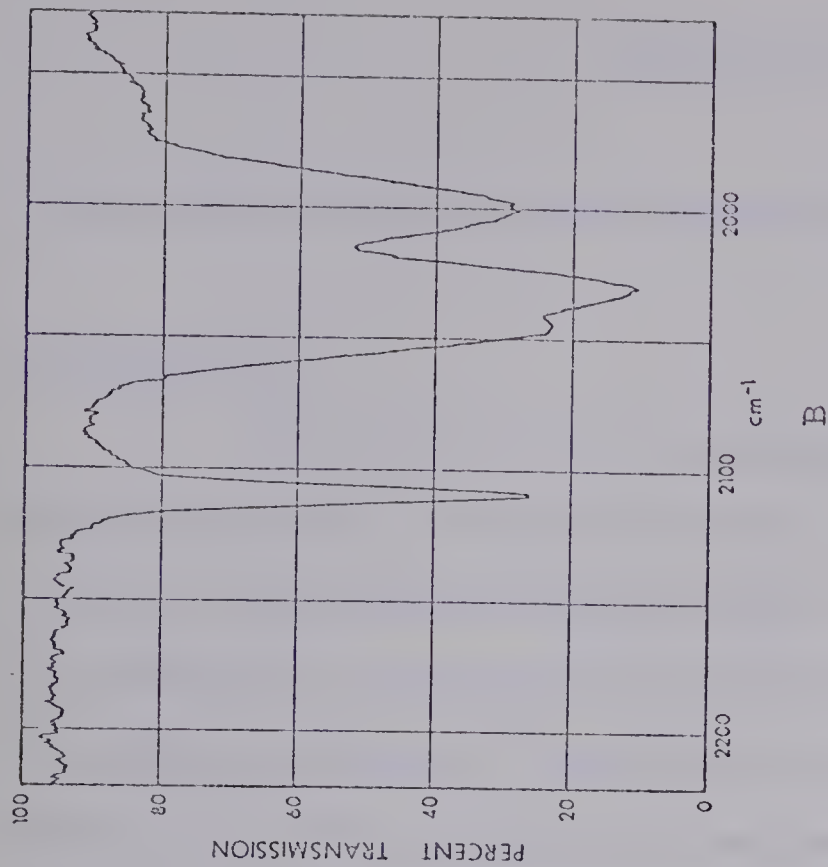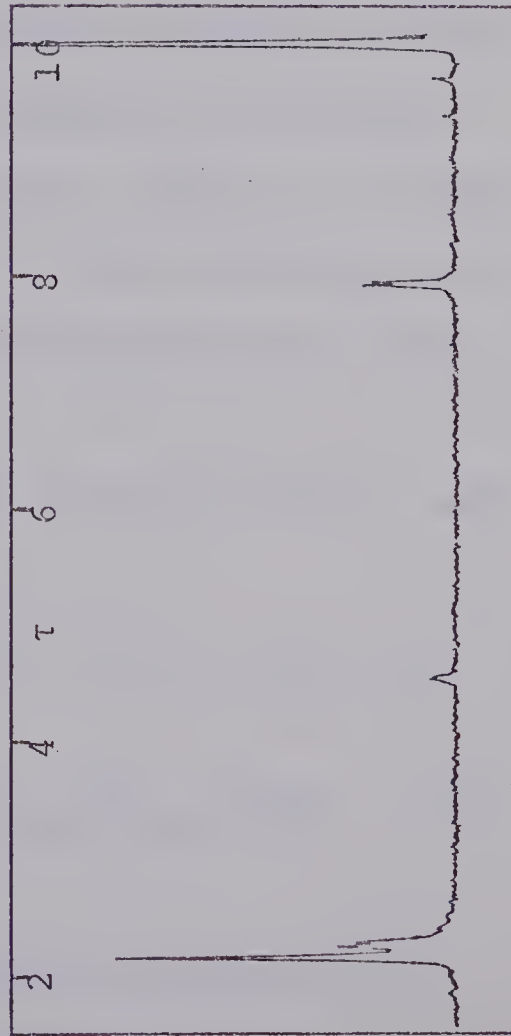
FIGURE II

A. Infrared spectrum of $[n\text{-}PrCNMn(CO)_5]^+$ $[PF_6]^-$. B. Infrared spectrum of $[n\text{-}PrCN\text{-}Mn(CO)_4PPh_3]^+[PF_6]^-$ in CH_2Cl_2. C. ^1H NMR spectrum of $[MeCNMn(CO)_4PPh_3]^+[PF_6]^-$ in CH_2Cl_2.

30.

CHAPTER II

REACTIONS OF SOME CATIONIC NITRILES OF MANGANESE CARBONYL

Introduction

The substitution reactions of the Group VII carbonyl cations do not appear to have been extensively studied. Although the hexacarbonyl cations, $[M(CO)_6]^+$, are inert to CO exchange[45], $[Re(CO)_6]^+$ exchanges oxygen with $H_2^{18}O$ [46]. The cation $[Re(CO)_6]^+$ will react with DPE to replace two CO groups, and with v-triars to replace three. Monodentate P(III) ligands do not react with $[Re(CO)_6]^+$ to yield substituted cations[2].

The hexacarbonyl and substituted carbonyl cations of Mn react with various anionic nucleophiles to produce salts or neutral species. The metathetical reaction of metal carbonyl anions with the Mn cations initially produces salts, which may then form compounds containing metal-metal bonds.

$$[Mn(CO)_6]^+ \ X^- + Na^+[Co(CO)_4]^- \longrightarrow (CO)_5Mn-Co(CO)_4 \quad (6)$$

Attack by methoxide ion can also produce neutral species.

$$[Mn(CO)_4(PPh_3)]^+ + OMe^- \longrightarrow Mn(CO)_3(PPh_3)_2COOMe \quad (47)$$

The reactions of substituted metal carbonyl cations with CN^- [48], and H^- [49] have also been reported.
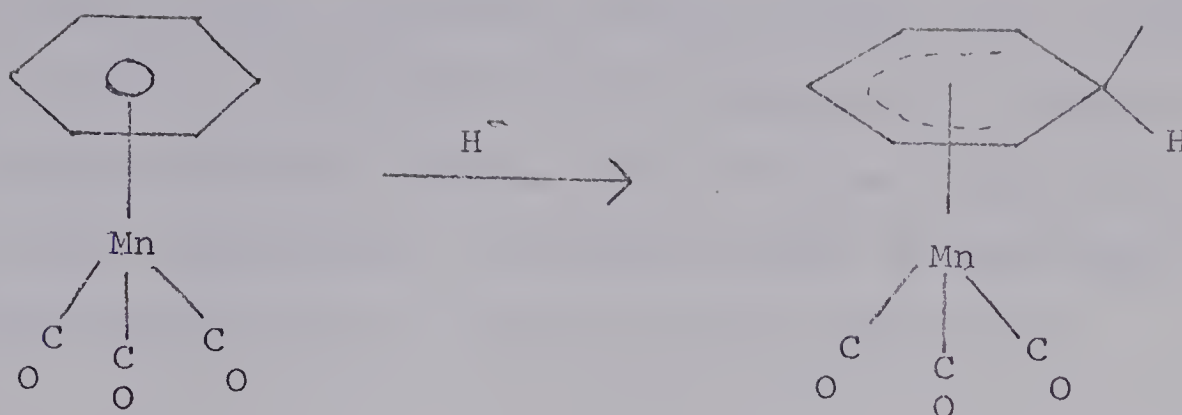
Generally, nitrile groups bonded to transition metals are extremely labile with respect to substitution. Many Pt isocyanide complexes can be prepared from $[Pt(NCMe)-(CNMe)(PPh_3)_2]^{2+}[BF_4]^-_2$ by facile replacement of MeCN by anionic and neutral ligands[50]. The compound bis-(benzo-nitrile) $PdCl_2$[51] is used as an intermediate in a wide range of synthetic applications. The MeCN groups in $(MeCN)_3M(CO)_3$ $(M = Cr,Mo,W)$[52] are also labile, and allow preparation of various sustituted-$M(CO)_3$ derivatives.

$$Me_3M'Cp + (MeCN)_3M(CO)_3 \longrightarrow CpM(CO)_3M'Me_3 \qquad (53)$$

$$M' = Ge,Sn; \quad M = Cr,Mo,W; \quad Cp = h^5-C_5H_5.$$

$$CpH + (MeCN)_3W(CO)_3 \longrightarrow CpW(CO)_3H \qquad (54)$$
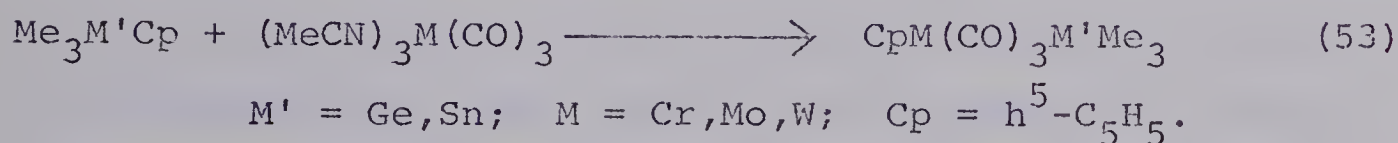
In this work, the reactions of the cationic nitriles of manganese carbonyl have been explored with respect to the above types of reaction, namely substitution reactions of CO and RCN, and reaction with anionic nucleophiles. In the substitution reactions of $[RCNMn(CO)_5]^+[PF_6]^-$ and $[RCN-$

$Mn(CO)_4PPh_3]^+[PF_6]^-$ with two electron donors such as PPh_3, the labilities of the MeCN and CO groups can be compared. It was thought that the nitrile group in these complexes would be labile, and provide a convenient route to other mono- and di-substituted salts by direct nitrile replacement.

Results and Discussion

It appears that both the RCN and CO groups in the compounds $[RCNMn(CO)_5]^+[PF_6]^-$ and $[RCNMn(CO)_4PPh_3]^+[PF_6]^-$ are generally inert in substitution reactions with other ligands. An exception to this generality is the reaction of $[MeCNMn(CO)_5]^+[PF_6]^-$ in refluxing MeCN to produce $[(MeCN)_3-Mn(CO)_3]^+[PF_6]^-$, a compound isoelectronic with the neutral $(MeCN)_3Cr(CO)_3$[52]. This reaction is discussed later.

The compound $[MeCNMn(CO)_5]^+[PF_6]^-$ does not react with $P(OCH_2)_3CEt$ on stirring in methylene chloride for 24 hours, nor does the salt react with PPh_3 in refluxing nitromethane. Heating the salt in refluxing mesitylene produces only decomposition. The reaction of $[t-BuCNMn(CO)_5]^+[PF_6]^-$ with PPh_3 in nitromethane produces only some decomposition upon UV irradiation for 9 hours.

Treatment of the disubstituted salt $[MeCNMn(CO)_4-PPh_3]^+[PF_6]^-$ with $AsPh_3$ or PPh_3 in boiling methylene chloride for 24 hours, with DPE in refluxing acetone for 14 hours, or with PPh_3 in refluxing nitromethane for 6 hours produces no reaction.

The reason for this inertness is not clear. The

positive charge on the metal may be the cause of the lack of lability, but the MeCN group in the [Pt(NCMe)(CNMe)-(PPh$_3$)$_2$]$^{2+}$ cation is labile. The parent carbonyl cation, [Mn(CO)$_6$]$^+$, is also rather inert, and does not exchange with CO[45].

The reaction with anionic nucleophiles does proceed for both types of derivative, but the products of the reaction appear to be too unstable to be isolated. Only in the case of NaI in hot acetone with [MeCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$ is a product isolated. This product is cis-Mn(CO)$_4$(PPh$_3$)I, isolated in low yield (10%), and characterized by infrared and mass spectroscopy. The salt [MeCNMn(CO)$_4$PPh$_3$]$^+$[PF$_6$]$^-$ reacts with (Me)$_2$CHNH$_2$, Tl acetylacetonate in methylene chloride, NaOMe in MeOH, KBH$_4$ in diglyme and Na$^+$[Co(CO)$_4$]$^-$ in tetrahydrofuran to produce products containing CO groups, but which decompose rapidly. The instability of these compounds may lie in the removal of the +1 charge on the metal atom; the MeCN group may then be labile as in the corresponding MeCNM(CO)$_5$ derivatives, so that decomposition occurs in the absence of a ligand to stabilize the product. However, if the reaction with OMe$^-$ in MeOH is repeated in the presence of PPh$_3$, no product of the form Mn(CO)$_3$(PPh$_3$)$_2$COOMe is observed.
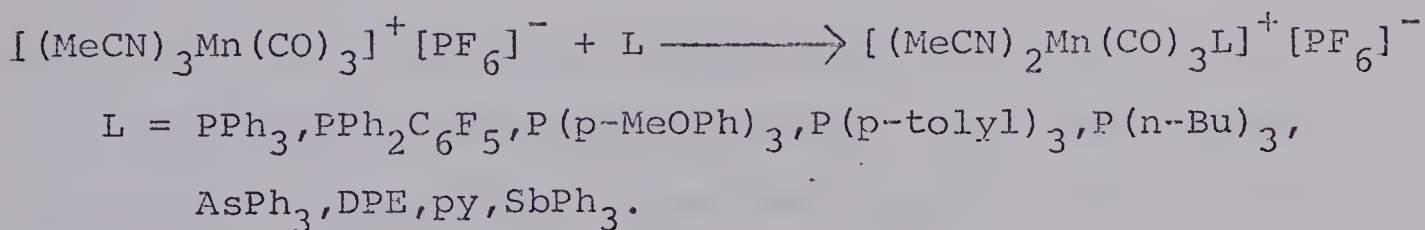
When [MeCNMn(CO)$_5$]$^+$[PF$_6$]$^-$ is heated under reflux in dry MeCN, the colourless solution gradually becomes deep orange in colour over the course of 3 hours. Removal of the solvent under reduced pressure affords a bright yellow, oily

residue. The infrared spectrum of this residue is consistent

with the formulation $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$, showing two

bands at 2064(s) and 1974(s,br) cm^{-1} in methylene chloride.

The band shapes are very similar to those of $(MeCN)_3W(CO)_3$[34]

and $(arene)M(CO)_3$[44]. The ^1H NMR spectrum is consistent with

the _cis_ isomer, showing a singlet at 7.93τ. What is more,

the solid reacts in a 1:1 molar ratio with $AsPh_3$ in nitro-

methane, without gas evolution, to form $[(MeCN)_2Mn(CO)_3$-

$AsPh_3]^+[PF_6]^-$, characterized fully by analysis, infrared and

NMR spectroscopy. Other ligands react in the same way as

$AsPh_3$. Repeated attempts to obtain crystals of $[(MeCN)_3Mn$-

$(CO)_3]^+[PF_6]^-$ from nitromethane, which would analyse corr-

ectly, failed. The reason for this may well be the dissoc-

iation of the salt in nitromethane to produce some free

nitrile, as shown by the infrared spectrum. Recrystalliz-

ation from methylene chloride produces better results, but

these are still not exact. Dissociation of the salt in meth-

ylene chloride is a much slower process; free MeCN can be

observed in the infrared after 24 hours. This could also ex-

plain the analytical results. A further point to include

here concerns the Raman spectrum of the derivative $[(MeCN)_2$-

$Mn(CO)_3P(p-tolyl)_3]^+[PF_6]^-$ in methylene chloride (Fig. IV).

If the spectrum is run after the sample has been prepared

for two days, a weak band is observed at 2255 cm^{-1}, and this

can be attributed to free MeCN. There is also a band at

2114(w) cm^{-1}. This may correspond to the strongly Raman

active B_1 mode of derivatives of the type $[RCNMn(CO)_5]^+[PF_6]^-$.

This could also explain the inexact analytical results for
$[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$ and indeed for some of the substitution derivatives.

The compound $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$ is best prepared by the addition of excess $NOPF_6$ to a suspension of $Mn_2(CO)_{10}$ in MeCN; this produces a mixture of $[MeCNMn(CO)_5]^+$ $[PF_6]^-, [Mn(CO)_6]^+[PF_6]^-$ and excess $NOPF_6$. If this mixture is then allowed to reflux in MeCN for 3 hours and the solvent removed under reduced pressure, the desired product can be obtained by extraction with methylene chloride. Removal of the solvent produces a bright yellow powder which is stable with respect to air oxidation for several days.

The compound $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$ reacts with a variety of ligands in nitromethane to replace a single MeCN group.

$$[(MeCN)_3Mn(CO)_3]^+[PF_6]^- + L \longrightarrow [(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$$

$$L = PPh_3, PPh_2C_6F_5, P(p\text{-}MeOPh)_3, P(p\text{-}tolyl)_3, P(n\text{-}Bu)_3,$$
$$AsPh_3, DPE, py, SbPh_3.$$

The reaction can be followed by infrared spectroscopy until the two strong bands of the starting material disappear. This takes about 4 hours at room temperature and appears to be independent of the nature and concentration of L. This suggests that the mechanism is a dissociative (S_N1) process. That is, the rate controlling step in the reaction is the dissociation of a MeCN group to produce a five coord-

inate intermediate which then rapidly reacts with the ligand L. This mechanism has been established for the isomerization and ligand exchange in the compound $Mn(CO)_3P_2Br$ (P = $P(OPh)_3$)[55]. A square-pyramidal intermediate would allow ligand exchange without isomerization; a trigonal-bipyramidal structure would also allow isomerization. It appears that in this substitution reaction, isomers are formed. This will be discussed later. The substitution reactions of the great majority of octahedral Mn complexes that have been studied proceed at a rate independant of the nature and concentration of the sustituting ligand, suggesting dissociative mechanisms[56]. In fact, octahedral complexes in general are considered to have a strong preference for a dissociative S_N1 mechanism in substitution reactions[57].

The substitution reaction of $[(MeCN)_3Mn(CO)_3]^+$ $[PF_6]^-$ in methylene chloride is much slower than in nitromethane. It is tempting to suggest solvent participation in the substitution reaction, especially since the infrared spectrum in nitromethane shows the presence of free nitrile and that in methylene chloride does not (except after several hours). However, kinetic studies of charged metal carbonyl complexes are uncommon and solvent effects difficult to assess[58].

The substitution compounds $[(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$ can be isolated in crystalline form only in the case of L = PPh_3, $AsPh_3$, py and $P(p-tolyl)_3$. In the case of L = $SbPh_3$, an equilibrium with $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$ is est-

ablished in solution, and the product cannot be separated.
In the case of other substitution products, solids can be
obtained, but these do not analyse correctly. This may be
due to the presence of impurities such as $[MeCNMn(CO)_5]^+$
$[PF_6]^-$ as mentioned earlier. The solids do, however, show
very similar infrared spectra to those fully characterized
derivatives. There is a tendency for these substitution pro-
ducts to form crystals in which solvent is retained in the
solvation sphere even after drying under high vacuum for
48 hours. This is illustrated in table VI.

The lability of only one MeCN group is shown by
the failure of $[(MeCN)_2Mn(CO)_3AsPh_3]^+[PF_6]^-$ to react with
excess $AsPh_3$ on stirring in nitromethane for 24 hours. Heat-
ing the solution at 60°C for 3 hours results in decomposition.
The salt $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$ reacts with PPh_3 in a 3:1
molar ratio to produce only the mono-substituted derivative
even at 60°C. Mesitylene would be expected to react with the
tris-nitrile complex to displace all the nitrile groups, but
no reaction occurs in nitromethane at 40°C. Also, in the
compound $[(MeCN)_2Mn(CO)_3DPE]^+[PF_6]^-$, the DPE coordinates
through one phosphorus only. This behaviour is unlike that
of $(MeCN)_3Cr(CO)_3$ in which all the MeCN moieties are labile[53].
The +1 charge on the metal may be responsible for this inert-
ness, since reaction with $[Et_4N]^+Cl^-$ initially produces a
similar infrared spectrum to that of the mono-substituted
derivatives, but the reaction continues to produce other
transient ν_{CO} before decomposition occurs. This behaviour

reflects that of $[RCNMn(CO)_4PPh_3]^+[PF_6]^-$ towards anionic nucleophiles.

It is interesting to note that when $[t\text{-}BuCNMn(CO)_5]^+$ $[PF_6]^-$ is allowed to reflux in t-BuCN, the infrared spectrum does show evidence of $[(t\text{-}BuCN)_3Mn(CO)_3]^+[PF_6]^-$ formation. The band positions are almost identical to those of the MeCN analogue, although the reaction is much slower (24 hours) as expected on the basis of steric hindrance. The analogous reaction with $[MeCNRe(CO)_5]^+[PF_6]^-$ does not occur even after refluxing in MeCN for 24 hours.

Infrared and Raman Spectra

The compound $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$ exhibits two strong carbonyl stretching modes in the infrared at 2064 and 1974(br) cm^{-1}. The higher frequency band is assigned as the A_1 mode and the lower one as the E mode in accordance with the usual procedure[44]. The compound also shows two weak peaks at 2323 and 2294 cm^{-1} which probably correspond to the C-N stretching modes. Further evidence for this is obtained from the Raman in methylene chloride; this shows bands of medium intensity at 2322 and 2296 cm^{-1}. The Raman of the carbonyl region is obscured because of fluorescence. The isoelectronic compound $(MeCN)_3Cr(CO)_3$ exhibits a C-N stretch at 2280 cm^{-1}. It is again assumed that the nitrile coordinates in an end-on rather than side-on fashion with the metal, through the nitrogen lone pair of electrons. A decrease in ν_{CN} with respect to the free ligand is attributed to side-on coordin-

ation in complexes containing Pt-nitrile-imine-ether link-
ages[59].

The infrared spectrum of $(MeCN)_3Cr(CO)_3$[36] shows
two ν_{CO} at 1910(s) and 1782(s) cm^{-1}. In the isoelectronic
compound $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$, the bands are substant-
ially higher at 2064(s) and 1974(s) cm^{-1}. This is a conse-
quence of the +1 charge on the metal; withdrawal of charge
into the CO π^* orbitals is substantially reduced and the
C-O bond strength increased.

Compounds of the type $[(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$ can
theoretically exist in 3 isomeric forms (Fig. III). All of
these forms would be expected to exhibit 3 infrared active
CO stretching modes.

A and C : C_s $2A'+A''$

B   : C_{2v} $2A_1+B_1$
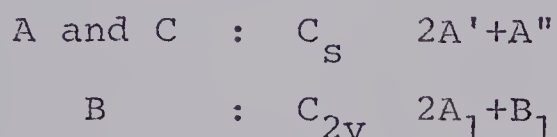
However, the ^1H NMR spectra of all the derivatives studied
show only one Me resonance, and this is consistent only with
structures A and B. It is not possible to distinguish between
A and B purely on the basis of band number in the infrared
or Raman $(3\nu_{CO}+2\nu_{CN})$; however, band intensities can be use-
fully analysed in this case. The infrared active CO stretch-
ing modes are shown in figure III. The _trans_ derivative corr-
esponds to isomer B and the _cis_ derivative to isomer A.
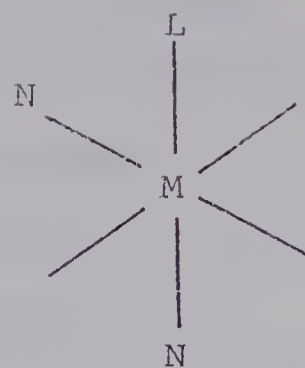
The A_1^b mode of the _trans_ isomer does not involve
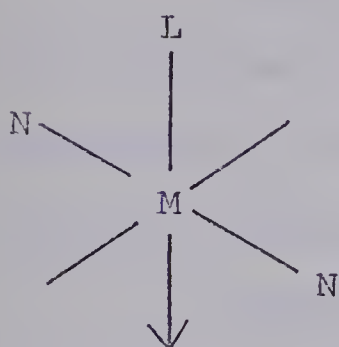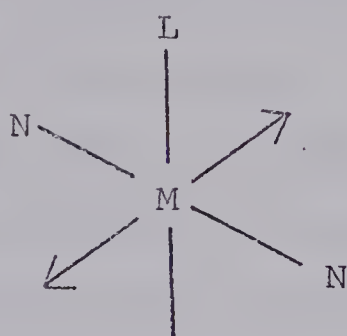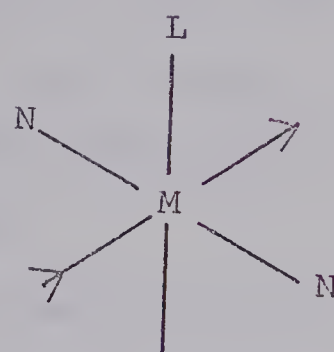a change of dipole moment, but is observed because of the
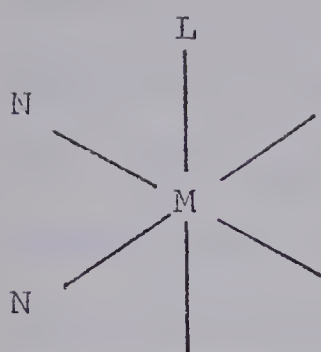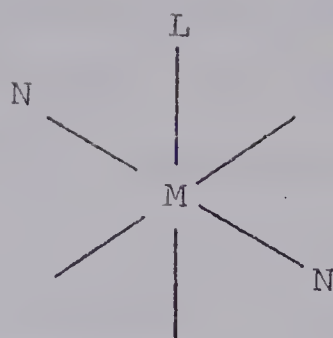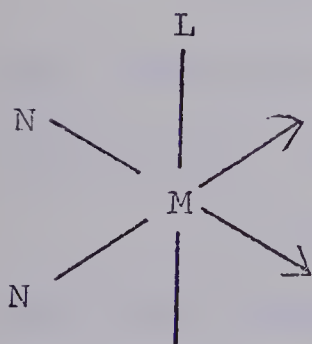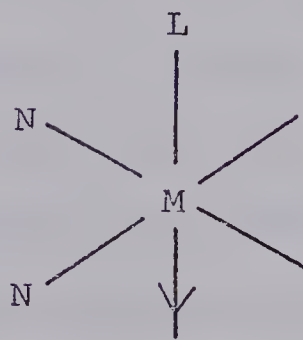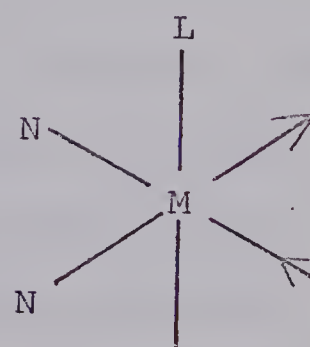
FIGURE III

The isomers and infrared active CO vibrations of the cations $[(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$.

distortion of the molecule from C_{2v} symmetry[60]. This symmetrical A_1^b mode should result in a weak infrared absorption only. The <u>cis</u> isomer allows substantial dipole moment changes for all modes and 3 strong bands are expected. This band pattern (s,s,s) is observed in <u>cis</u>-Mn(CO)$_3$P$_2$Br, P = P(OPh)$_3$, and the other pattern (w,s,s) for the <u>trans</u> isomer[61]. This is in agreement with the predictions of the Cotton-Kraihanzel theory[62,63,64].

The derivatives [(MeCN)$_2$Mn(CO)$_3$L]$^+$[PF$_6$]$^-$ which have been isolated and characterized show 3 strong ν_{CO}, and are concluded to be the <u>cis</u> isomer, A. Dipole moment measurements would be required to confirm such a conclusion.

However, a fourth band is generally observed in the infrared spectrum of the reaction mixture as a weak shoulder to the low frequency side of the highest ν_{CO}. This is thought to correspond to the <u>trans</u> isomer.

A mixture of the <u>cis</u> and <u>trans</u> isomers of Mn(CO)$_3$-P$_2$Br shows only four bands at 2070(w), 2053(s), 2000(s), and 1949(s) cm^{-1}; the lower two bands for each isomer coincide.

In the preparation of [(MeCN)$_2$Mn(CO)$_3$PPh$_3$]$^+$[PF$_6$]$^-$, the first crystallization produces yellow needles which exhibit infrared active bands at 2055(s), 2042(w,sh), 1980(s) and 1953(s) cm^{-1}. These crystals analyse correctly as [(MeCN)$_2$Mn(CO)$_3$PPh$_3$]$^+$[PF$_6$]$^-$.1/2CH$_3$NO$_2$. Recrystallization from nitromethane/diethyl ether produces yellow needles with bands at 2054(s), 1982(s) and 1953(s) cm^{-1}, which also analyse as the above derivative. The mother liquor shows bands at 2054

(w), 2043(w), 1975(m) and 1951(m) cm^{-1}. The assignment is therefore made as:-

cis   :   2055, 1982 and 1953 cm^{-1}

trans :   2042, 1975 and 1951 cm^{-1}.

Similar arguments can be applied to the other substitution derivatives.

On the basis of the Graham σ/π parameter scale[65], acetonitrile functions as a π-donor in complexes of type LMo(CO)$_5$. Cotton, on the other hand, believes acetonitrile to be a weak π-acceptor[64]. In either case, where L is a phosphine or arsine, the π-acceptor property of L will be much greater than that of acetonitrile. This means that, on the basis of the trans effect, the highest carbonyl stretching mode will be that trans to the L group, namely A'$_b$. The intensity of the other two bands is about twice that of the A'$_b$ mode as expected.

Since the intensity of the highest ν_{CO} of the trans isomer is weak, and that of the cis isomer strong, no estimate of the relative amounts of isomers can be made. The isomers cannot be separated by chromatography because the salts become bound to the column material (florisil).

No interconversion of isomers (L = AsPh$_3$) occurs on warming the cis isomer in nitromethane at 60°C for 3 hours. The higher stability of the cis isomer may be attributed to strong M-C π-bonding. The 3 CO groups compete for the metal d$_\pi$ orbitals with the AsPh$_3$ and the poorly π-accepting MeCN groups. In the trans derivative, two CO groups must

share the same d_π orbital, resulting in weaker M-C bonds. Steric effects would tend to favour the trans isomer, but in this case the MeCN moiety appears to be small enough to allow formation of the cis derivative in substantial quantities without steric crowding.

In the infrared spectrum of the derivatives $[(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$, two weak bands are observed around 2300 cm^{-1}. These are believed to be the two ν_{CN} expected from this stoichiometry. The Raman spectrum of the P(p-tolyl)$_3$ compound in methylene chloride shows two bands at 2320(m) and 2292(vs) cm^{-1}, consistent with the above assignment. The infrared spectra are shown in table VII, and the Raman spectrum of the P(p-tolyl)$_3$ derivative in figure IV.

The infrared spectra of the compounds $[(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$, L = PPh$_3$,PPh$_2C_6F_5$,P(p-tolyl)$_3$,P(p-MeOPh)$_3$ and P(n-Bu)$_3$ reflect the σ-donor and π-acceptor properties of the ligand L. P(n-Bu)$_3$ would be expected to be the best σ-donor and poorest π-acceptor of the ligand L; this results in strong M-C π bonds, and consequently lower ν_{CO}. Both P(p-tolyl)$_3$ and P(p-MeOPh)$_3$ are expected to be poorer π-acceptors than PPh$_3$. The inductively donating Me groups would make P(p-tolyl)$_3$ a better σ-donor than PPh$_3$, and this tends to lower the π-acceptor property of the ligand. The MeO groups in P(p-MeOPh)$_3$ are expected to be inductively withdrawing, but would be expected to supplement the π-charge of the rings by the resonance form shown below.

P — ⁻⟨═══⟩═O⁺ ----- Me
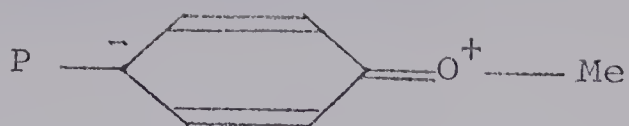
This would make the ligand a poorer π-acceptor

than PPh_3, consistent with the lower ν_{CO}.

The ligand $PPh_2C_6F_5$ appears to be a much better

π-acceptor than PPh_3, since the ν_{CO} in this compound are

higher than in the PPh_3 derivative.

Conductivities

The molar conductivities of $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$

and the substitution products $[(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$ are

of the order expected of 1:1 salts[31]. The conductivities can

be measured in nitromethane if the solutions are made up

immediately before measurements are made. In this way, any

dissociation of MeCN which may occur is minimal. The molar

conductivities are shown in table IX.

NMR Spectra

Assignment of the ^{1}H NMR spectra of the derivatives

$[(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$ is routine. Solvent, present in the

solvation sphere, is also observed in the spectra. All sig-

nals are sharp except for the pyridine derivative. P-H coup-

ling, observed earlier in cis-$[(MeCN)Mn(CO)_4PPh_3]^+[PF_6]^-$, is

again present in $[(MeCN)_2Mn(CO)_3]^+[PF_6]^-$. Chemical shifts

are shown in table VIII.

are shown in table VIII.

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Solvents were dried as described previously. Microanalyses, infrared and NMR spectra were obtained in the manner previously mentioned.

Preparation of $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$

An excess of $NOPF_6$ (65 mmoles), dissolved in MeCN (50ml) was added through a dropping funnel to a suspension of $Mn_2(CO)_{10}$ (11.7g., 30 mmoles) in the same solvent (100ml). The addition of the $NOPF_6$ must be slow to minimize the formation of $[Mn(CO)_6]^+[PF_6]^-$. Over the addition time (3 hours), the solution changed colour from yellow to light green. The solution was then refluxed under nitrogen for 3 hours, the solution again changing colour to dark orange. The solvent was removed under reduced pressure, and the yellow residue extracted with methylene chloride (2 x 50ml), and the solution filtered through a medium-pore sinter. Removal of the solvent under reduced pressure affords a yellow powder of $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$. The solid is air-stable and soluble in methylene chloride without decomposition, except after several hours. The infrared spectrum in nitromethane, however, shows the presence of free MeCN. The physical and spectroscopic data for this compound are given in tables VI-IX.

Preparation of $[(MeCN)_2Mn(CO)_3L]^+[PF_6]^-$; $L = PPh_3$, $AsPh_3$, py, DPE, $P(p\text{-}tolyl)_3$, $P(p\text{-}MeOPh)_3$, $P(n\text{-}Bu)_3$, $PPh_2C_6F_5$.

The compound $[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$ (2.0g., 5 mmoles) was dissolved in nitromethane (50ml), and a slight excess of L added. The mixture was stirred for about 4 hours and the reaction followed by infrared spectroscopy until the bands due to the starting material disappeared. In the case of $L = P(p\text{-}tolyl)_3$ and $P(p\text{-}MeOPh)_3$ the yellow solution became deep red in colour; in the other cases the solution changed to an orange colour. When the reaction was completed, the solution was filtered and reduced to small bulk under reduced pressure. Addition of diethyl ether (75ml) and cooling to -20°C produced crystals of product. The $P(p\text{-}tolyl)_3$ derivative was obtained as cubic crystals, the PPh_3, py and $AsPh_3$ compounds as needles and the remainder as powders. No solid samples of the $P(n\text{-}Bu)_3$ and $P(p\text{-}MeOPh)_3$ derivatives could be obtained. The salts showed varying amounts of solvent inclusion in the solvation spheres, even after drying for 48 hours. This solvent was detected in the ^1H NMR spectra except for the py derivative, for which very broad signals were obtained. The physical and spectroscopic properties of these compounds are shown in tables VI-IX.

TABLE VI

Analytical Data and Physical Properties

Compound	Calculated %			Found %			Yield %	Colour	M.p. °C
	C	H	N	C	H	N			
$[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$	26.55	2.23	10.32	25.45	2.57	9.18	60	Yellow	....
$[(MeCN)_2Mn(CO)_3PPh_3]^+[PF_6]^-$ .1/2CH$_3$NO$_2$	46.49	3.44	5.31	46.77	3.63	5.23	72	Yellow	Dec 165
$[(MeCN)_2Mn(CO)_3AsPh_3]^+[PF_6]^-$	44.66	3.15	4.17	44.53	3.79	4.02	84	Yellow	Dec 169
$[(MeCN)_2Mn(CO)_3P(p-tolyl)_3]^+$ $[PF_6]^-$ .1/2C$_4$H$_{10}$O	50.86	4.70	3.95	50.60	4.94	4.18	51	Yellow	118-120
$[(MeCN)_2Mn(CO)_3py]^+[PF_6]^-$	37.01	4.07	8.09	36.92	2.91	7.76	36	Light Brown	Dec 125

TABLE VII

Infrared Data[a]

Compound[b]	ν_{CN}		ν_{CO} cm^{-1}			
[(MeCN)₃Mn(CO)₃]⁺[PF₆]⁻	2323(w)	2294(w)	2064(s)	1974(s,br)		
[(MeCN)₂Mn(CO)₃PPh₃]⁺[PF₆]⁻		2290(w)	2055(s)ᵇ	2043(w,sh)ᶜ	1981(s)	1952(s)
[(MeCN)₂Mn(CO)₃AsPh₃]⁺[PF₆]⁻	2321(w)	2290(w)	2056(s)	2038(w,sh)	1981(s)	1957(s)
[(MeCN)₂Mn(CO)₃SbPh₃]⁺[PF₆]⁻	2320(w)	2285(w)	2053(s)	2040(w,sh)	1980(s)	1958(s)
[(MeCN)₂Mn(CO)₃py]⁺[PF₆]⁻	2318(w)	2288(w)	2049(s)	2042(w,sh)	1959(s)	1952(s)
[(MeCN)₂Mn(CO)₃P(p-tolyl)₃]⁺[PF₆]⁻	2320(w)	2292(w)	2053(s)	2038(w,sh)	1979(s)	1950(s)
[(MeCN)₂Mn(CO)₃P(p-MeOPh)₃]⁺[PF₆]⁻	2319(w)	2291(w)	2052(s)	2034(w,sh)	1975(s)	1949(s)
[(MeCN)₂Mn(CO)₃DPE]⁺[PF₆]⁻	2325(w)	2284(w)	2041(s)		1973(s)	1953(s)
[(MeCN)₂Mn(CO)₃PPh₂C₆F₅]⁺[PF₆]⁻	2321(w)	2287(w)	2063(s)	2043(w)	1992(s)	1963(s)
[(MeCN)₂Mn(CO)₃P(n-Bu)₃]⁺[PF₆]⁻	2320(w)	2283(w)	2032(s)	2021(w)	1958(s)	1941(s)

[a]Recorded in nitromethane.   [b]Values in this column correspond to the <u>cis</u> isomer.

[c]Values in this column correspond to the <u>trans</u> isomer.

TABLE VIII

^{1}H NMR Spectral Data^a

Compound	τ
$[(MeCN)_3Mn(CO)_3]^+[PF_6]^-$	7.63 singlet (Me)
$[(MeCN)_2Mn(CO)_3PPh_3]^+[PF_6]^-$ $\cdot 1/2CH_3NO_2$	7.99 doublet (Me), 2.43 complex (Ph), 5.68 singlet (CH$_3$NO$_2$), J_{P-H} = 3.0 c.p.s.
$[(MeCN)_2Mn(CO)_3AsPh_3]^+[PF_6]^-$	7.97 singlet (Me), 2.46 complex (Ph)
$[(MeCN)_2Mn(CO)_3DPE]^+[PF_6]^{-b}$	8.62, 8.08 broad (CH$_2$), 2.52 complex (Ph)^c
$[(MeCN)_2Mn(CO)_3py]^+[PF_6]^-$	7.52 singlet (Me), 2.45,2.04,1.61 complex (py)^d
$[(MeCN)_2Mn(CO)_3P(p-tolyl)_3]^+$ $[PF_6]^- \cdot 1/2C_4H_{10}O$	8.00 singlet (MeCN), 7.63 singlet (Me),2.65 complex (Ph), 8.87 triplet, 6.56 quartet (Et$_2$O)
$[(MeCN)_2Mn(CO)_3PPh_2C_6F_5]^+$ $[PF_6]^-$	7.84 singlet (Me), 2.44 complex (Ph)

^{a}Recorded in CD$_2$Cl$_2$ unless otherwise noted. ^{b}DPE = Ph$_2$PCH$_2$CH$_2$PPh$_2$.

^{c}Poor spectrum recorded in CD$_3$CN. ^{d}No spectrum could be obtained in CD$_3$NO$_2$.

52.

TABLE IX

Conductivity Data[a]

Compound	Solution conc. (mM)	Molar Conductivity (mhos cm^2 mole^{-1})	Temperature (°C)
[(MeCN)$_3$Mn(CO)$_3$]$^+$[PF$_6$]$^-$	0.91	95.0	25.0
[(MeCN)$_2$Mn(CO)$_3$PPh$_3$]$^+$[PF$_6$]$^-$	0.92	89.6	25.0
[(MeCN)$_2$Mn(CO)$_3$AsPh$_3$]$^+$[PF$_6$]$^-$	1.07	83.9	24.8
[(MeCN)$_2$Mn(CO)$_3$P(p-tolyl)$_3$]$^+$[PF$_6$]$^-$	1.15	81.2	24.6
[(MeCN)$_2$Mn(CO)$_3$py]$^+$[PF$_6$]$^-$	0.95	85.3	24.8

[a]Recorded in nitromethane.
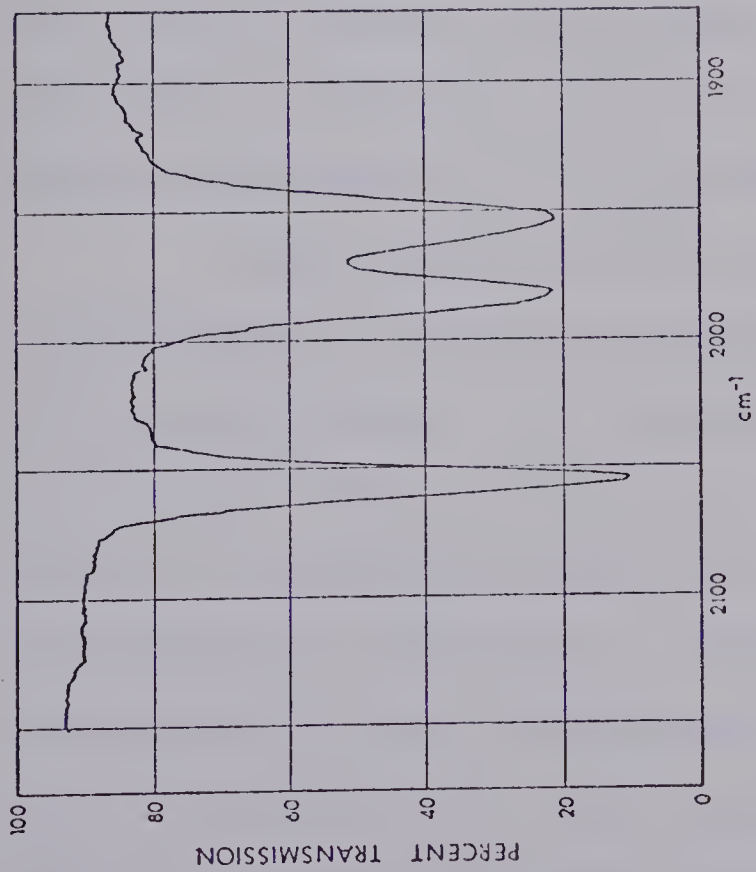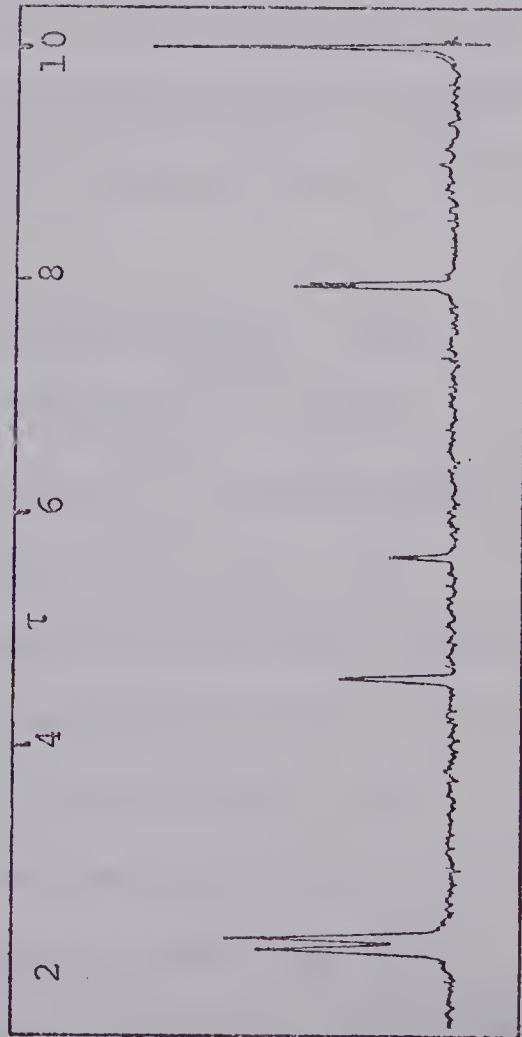
FIGURE IV

A. Infrared spectrum of [(MeCN)$_2$Mn-(CO)$_3$PPh$_3$]$^+$[PF$_6$]$^-$ in nitromethane.

B. Raman spectrum of [(MeCN)$_2$Mn(CO)$_3$-P(p-tolyl)$_3$]$^+$[PF$_6$]$^-$ in CH$_2$Cl$_2$. C. ^{1}H NMR spectrum of A in CH$_2$Cl$_2$.

CHAPTER III

SOME REACTIONS OF THE h^5-CYCLOPENTADIENYLDICARBONYL-
NITROSYL CATION OF RHENIUM

The reaction of $[h^5$-$C_5H_5Re(CO)_2NO]^+[PF_6]^-$ with $[n$-$Bu_4N]^+Br^-$ in acetone at room temperature produces a mixture of products which can be separated by chromatography on alumina. One of the products is the bromide, h^5-$C_5H_5Re(CO)(NO)Br$, characterized by analysis and by infrared and mass spectrometry. This compound should exist in enantiomeric forms. The mass spectrum is shown in table X, and shows initial CO loss followed by NO loss.

A small amount of yellow oil is also obtained from the reaction mixture. This shows two infrared active stretching modes in methylene chloride at 1775(s) and 1725(s) cm^{-1}, and may correspond to h^5-$C_5H_5Re(NO)_2$.

The reaction of $[h^5$-$C_5H_5Re(CO)_2NO]^+[PF_6]^-$ with triethylamine in acetone was found by Okamoto[21] to give $[h^5C_5H_5Re(CO)(NO)]_2$ in an analogous manner to the manganese derivative[66]. When this reaction is repeated using 'wet' acetone, a colourless liquid can be isolated from the reaction mixture by sublimation. The mass spectrum of this liquid corresponds to the stoichiometry h^5-$C_5H_5Re(CO)(NO)H$, and shows concurrent loss of CO and NO from the parent ion. The infrared spectrum shows two strong bands at 1980 and 1722 cm^{-1}, corresponding to ν_{CO} and ν_{NO} respectively. No infrared

active Re-H stretch is observed. The ^{1}H NMR spectrum shows
a singlet at 4.8τ corresponding to C_5H_5, and a weak hydride
resonance at 18τ. The full characterization of this hydride
has been completed by R.P. Stewart of this department[68].
This hydride is also expected to be optically active.

EXPERIMENTAL

Spectra were recorded under the same conditions shown in Chapter I.

Rhenium carbonyl was converted to $h^5-C_5H_5Re(CO)_3$ by refluxing with dicyclopentadiene[67]. This was converted to $[h^5-C_5H_5Re(CO)_2NO]^+[PF_6]^-$ by the method of Okamoto[21].

Preparation of $h^5-C_5H_5Re(CO)(NO)Br$

$[h^5-C_5H_5Re(CO)_2NO]^+[PF_6]^-$ (0.48g.,1.2 mmoles) and $[n-Bu_4N]^+Br^-$ (1.2 mmoles) were dissolved in acetone (50ml) and the mixture stirred magnetically for about 24 hours under a nitrogen atmosphere. The solution gradually changed colour from yellow to dark red. The solvent was then removed under reduced pressure, and the remaining solid chromato-graphed on alumina under nitrogen. Elution with methylene chloride gave two fractions. The first afforded a small amount of yellow oil upon removal of solvent and may corres-pond to $h^5-C_5H_5Re(NO)_2$, as described. The second fraction was a dark red solution. Removal of solvent on a rotary evapor-ator followed by sublimation onto a water-cooled probe (0.3mm Hg at 50°C) provided a dark red solid in low yield (14%), which analysed as $h^5-C_5H_5Re(CO)(NO)Br$.

Calculated: C 18.50, H 3.60, N 1.30%

Found   : C 18.63, H 3.91, N 1.33%.

The solid melted sharply at 114-115°C, and exhib-

ited infrared active bands at 1998(s) and 1736(s) cm^{-1}, in

methylene chloride, corresponding to ν_{CO} and ν_{NO} respect-

ively. The mass spectrum is shown in table X, and shows a

pattern typical of $^{79}Br/^{81}Br$ and $^{185}Re/^{187}Re$.

Evidence for $h^5-C_5H_5Re(CO)(NO)H$

$[h^5-C_5H_5Re(CO)_2(NO)]^+[PF_6]^-$ (2.0g., 4.2 mmoles)

was dissolved in 50ml. of 'wet' acetone and treated with 2ml

of triethylamine. An immediate colour change from yellow to

dark red was observed. After refluxing for 30 minutes, the

solvent was removed under reduced pressure and the residue

chromatographed on alumina using acetone as eluant. The first

red band gave a yellow solution which afforded a yellow-

brown solid on removal of solvent under vacuum. A colour-

less liquid was sublimed (0.1mm Hg at 100°C) from the

residue onto a solid CO_2 probe. The infrared spectrum of

this liquid exhibited two bands at 1980(s) and 1722(s) cm^{-1},

corresponding to ν_{CO} and ν_{NO} respectively. The mass spectrum

of this liquid is shown in table X. The NMR spectrum shows

absorptions at 4.8τ (C_5H_5) and a weak absorption at 18τ (H) in

$CDCl_3$.

TABLE X

MASS SPECTRA DATA

$h^5-C_5H_5Re(CO)(NO)Br$

m/e^a	Ion
389	$CpRe(CO)(NO)Br^{+b}$
361	$CpRe(NO)Br^+$
331	$CpReBr^+$
305	$ReBrC_3H_3^+$
279	$ReBrCH^+$
266	$ReBr^+$
224	ReC_3H^+
200	$ReCH^+$
194.5	$CpRe(CO)(NO)Br^{2+}$
187	Re^+
180.5	$CpRe(NO)Br^{2+}$
165.5	$CpReBr^{2+}$

$h^5-C_5H_5Re(CO)(NO)H$

311	$CpRe(CO)(NO)H^+$
283	$CpRe(NO)H^+$
281	$CpRe(CO)H^+$
253	$CpReH^+$
224	ReC_3H^+
187	Re^+

^{a}m/e values for ^{187}Re and ^{79}Br containing ions.

^{b}Cp = $h^5-C_5H_5$.

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